Structural, Thermodynamic, and Educational Considerations in Self-Assembly

by

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DEDICATION

For Papa.

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ABSTRACT

In molecular self-assembly, both structure and thermodynamics are critical in monolayer formation. The potential for generating complexity in self-assembled system was explored in two-dimensions by investigating the two-dimensional crystals formed from a series of multicarboxylated arenes related to trimesic acid at the heptanoic acid/highly ordered pyrolytic graphite interface. In the molecular design strategy for this series, phenylene spacers were added between the central phenylene core and one or more of the carboxylic acids of trimesic acid. By this design strategy, monolayers in multiple plane groups and one example of a disordered phase were obtained for this series. The composition of the dimers in the two-dimensional monolayers mirrors the composition of the carboxylates at metal centers in microporous coordination polymers incorporating these carboxylated arenes as organic linkers suggesting spacers as a promising design tool.

To directly explore the thermodynamics of monolayer self-assembly, experimental heats of adsorption from solution onto powdered graphite were measured using flow microcalorimetry for a series of aliphatic adsorbates varying in their terminal functional group. Monolayer structure for each adsorbate is known from the scanning tunneling microscopy literature. Comparing these experimental values to computationally derived lattice energies for this series, the ordering of the enthalpies of adsorption and lattice energies did not match when pre-assembly in solution or strong solvent-analyte interactions were not accounted for by the gas-phase, computationally derived lattice energies. Such findings have important implications for systems, such as industrial separations, which rely on selective adsorption from solution.

While there are increased calls for more active learning opportunities in post-secondary classrooms, little is known about how to effectively teach active learning strategies. To address this need, a semester-long, active learning professional development program was designed for graduate student instructors (GSIs) teaching general chemistry lecture discussion sections to introduce the graduate student instructors to active learning strategies which they would then embed in their discussion sections. The GSIs valued practice in authentic instructor responsibilities and exhibited a range in understanding and implementation of active learning strategies. Long-term, ongoing professional development of individuals remains critical in instructional reform.

Chapter 1

Introduction

Self-Assembly

In self-assembly, pre-existing, distinct components come together into a defined arrangement without external direction. Additional constraints to this definition include limiting to reversible processes controlled through strategic design of the components.[1] Self-assembly is a well represented phenomenon in nature (e.g. sand dunes, schools of fish, clouds) and the field of molecular self-assembly includes not only areas of chemistry, but also disciplines such as biology, materials science, engineering, and physics. Molecular self-assembly in particular has been successfully exploited for rational design of bottom-up nanoarchitectures. Unlike molecular synthesis, self-assembly relies extensively on relatively weak noncovalent interactions. Such molecular self-assemblies allow for unprecedented exploration of the influence intermolecular interactions which influence the self-assembly pattern.

Structure and Self-Assembled Systems

Self-assembly at the liquid/solid interface is important for applications such as lubrication, nanofabrication, separations, and surface functionalization. While chemisorbed monolayers (namely, those relying on thiol-gold chemistry) are a large class of self-assembled monolayers, the focus here is on physisorbed SAMs. Physisorbed monolayers have been of interest since monolayers were discovered.[2] One technique which has been highly effective in revealing the molecular patterns of physisorbed SAMs is scanning tunneling microscopy (STM). Binnig and Rohrer won the 1986 Nobel Prize in physics for their design of the STM.[3] STM is especially powerful because it can reveal both periodic and aperiodic assemblies. Investigations of physisorbed monolayers are often pursued on atomically flat substrates such as highly ordered pyrolytic graphite (HOPG), gold, or MoS_2. HOPG is the most common substrate for STM imaging because it is atomically flat, conductive, and obtaining a fresh surface for adsorption requires only cleaving the surface with tape. The close registry between the methylene bond lengths and the center of the rings in the basal planes makes HOPG an especially good substrate for adsorbents with alkyl chains. While solvent[4–6] and substrate[7–9] choice are important variables in supramolecular patterning (Figure 1-1), other factors contributing to the patterning of a single-component monolayer include concentration[6,10–12] and thermal history.[13]

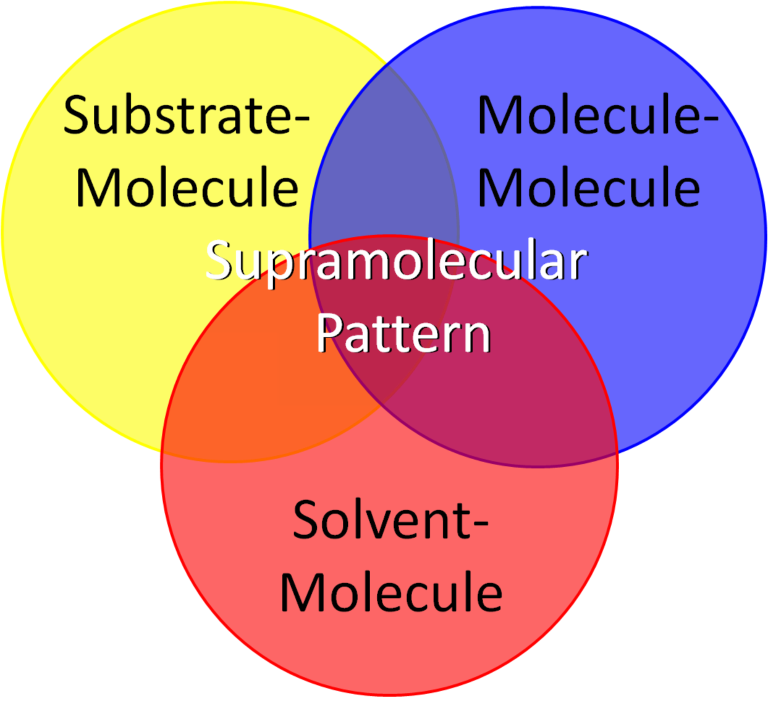

Figure 1-1 Venn diagram highlighting the interplay of substrate-molecule, molecule-molecule, and solvent-molecule interactions in monolayer patterning at the solution/solid interface.

In a typical STM imaging experiment, a few microliters of solution are placed on a freshly cleaved HOPG substrate. A monolayer spontaneously forms at the solution/solid interface. An ideal solvent for STM imaging has low volatility and a reasonable ability to dissolve a given compound, although monolayer formation has been reported from solvophobic conditions.[14] Low volatility is critical so that the solution concentration does not change during imaging, and so that multilayers and kinetic or metastable phases are not formed. Common solvents include phenyloctane, heptanoic acid, and 1,2,4-trichlorobenzene depending on the system at hand. A thin piece of metal wire (e.g. Pt/Ir or W) is cut, attached to the tip control unit, and submerged in the solution. During imaging, a voltage bias is applied between the metal tip and the conductive substrate allowing electrons to tunnel between the tip and the substrate. The resulting current is measured as the tip is rastered along the substrate by piezoelectrics in the tip controller. The image is formed from the difference in tunneling efficiency through different adsorbates; for example, aromatic moieties appear bright and methylenes appear relatively dark. The contrast of different terminal functional groups has been correlated to both topographic effects and analyte-substrate electronic coupling suggesting a fine interplay of topographic and electronic effects in interpreting STM images.[15]

Motivation to Study Monolayer Structure

Beyond the beautiful images and the ability to image in real time and space, STM enables exploration of supramolecular structure in two-dimensions (2D) with relevance to three-dimensional (3D) crystal engineering. 3D crystals can form in one of 270 space groups, but 2D crystals can assemble into only one of 17 distinct plane groups. The 2D crystal systems are inherently simpler than 3D systems. This reduced dimensionality allows fundamental questions of crystallization and self-assembly to be addressed and explored without some of the challenges in 3D crystallization.

The Matzger lab has brought the language of crystallography to the discussion of physisorbed SAMs.[16] One reoccurring theme in our work with physisorbed SAMs has been to use the 2D crystals as model systems to understand bulk crystallization. Recently, we have done the reverse and applied a successful strategy from 3D microporous coordination polymers (MCPs) to 2D crystallization. One persistent issue in MCP structures has been interpenetration, growth of one network in the voice space of another which results in partial/full blockage of the network pores. To overcome this issue, reduced symmetry organic linkers have been shown to successfully thwart interpenetration and therefore preserve the large pores in the MCPs.[17] Two routes to reduced symmetry have been reported for these multicarboxylated arenes: varying the number or position of the carboxylic acid and asymmetric addition of phenylene spacers.[18] 2D crystals of the analytes from the first strategy have shown that the geometry of the available hydrogen bonding interactions controlled the 2D crystal structure and thus porosity. The first strategy also showed that reducing the linker symmetry within the series does not necessarily change the plane group of the monolayer.[19] It is unclear thus far if these findings are limited to this route to symmetry reduction, or can be extended to other strategies. The second strategy, asymmetric addition of phenylene spacers, is explored in 2D self-assembly in chapter 2 of this thesis.

Thermodynamics in Self-Assembled Monolayers

Motivation

As is true in 3D crystallization, crystallization in 2D is influenced by both kinetic and thermodynamic factors and structural considerations can only provide so much insight. An example of a situation where understanding of the role of thermodynamics in 2D crystallization is critical is competitive adsorption. From a mixture in solution, several possible outcomes are possible: preferential adsorption,[20,21] cocrystallization,[22–27] and phase segregation.[28,29] Relative concentrations and adsorbate identities are crucial factors in dictating the resulting crystal, but predicting the outcome is hampered by a lack of understanding of the thermodynamics factors in SAM formation. A number of recent investigations have probed the role of temperature and concentration in phase transformation[13,30] and opening and closing of pores[31] by STM and computational investigations.[32] The Matzger lab has advanced our understanding of thermodynamic factors by which physisorbed monolayers self-assemble by deriving the differences in free energies of phase segregated monolayers[33] and using additives to stabilize meta-stable monolayer assemblies.[34] Differential scanning calorimetry[35–38] and temperature programmed desorption[39] are also powerful ways to access thermodynamics of monolayer formation. While each of these studies has added to our understanding of thermodynamic roles within self-assembly, such approaches are either limited to the system studied or far removed from systems of interest.

Flow Microcalorimetry

The general lack of understanding of the thermodynamics of monolayer formation is ironic because early evidence for monolayer formation came from calorimetry investigations.[2,40] The Matzger lab has recently obtained a flow microcalorimeter to quantitatively investigate thermodynamics factors related to adsorption. In flow microcalorimetry, a powdered sorbent is placed in the thermodynamic cell (Figure 1-2) and a background fluid is pumped into, through, and out of the cell. The thermistor measures the thermal signal in the cell. After the cell is in thermal equilibrium with the sorbent and flowing fluid (as evidenced by a constant thermal output), the cell is calibrated by pulsing a known amount of energy and the software integrates the response against the baseline. The solution of known concentration and composition is then flowed through the thermal cell and the measured response is integrated against the baseline. Additional instrumental details can be found in chapter 3.

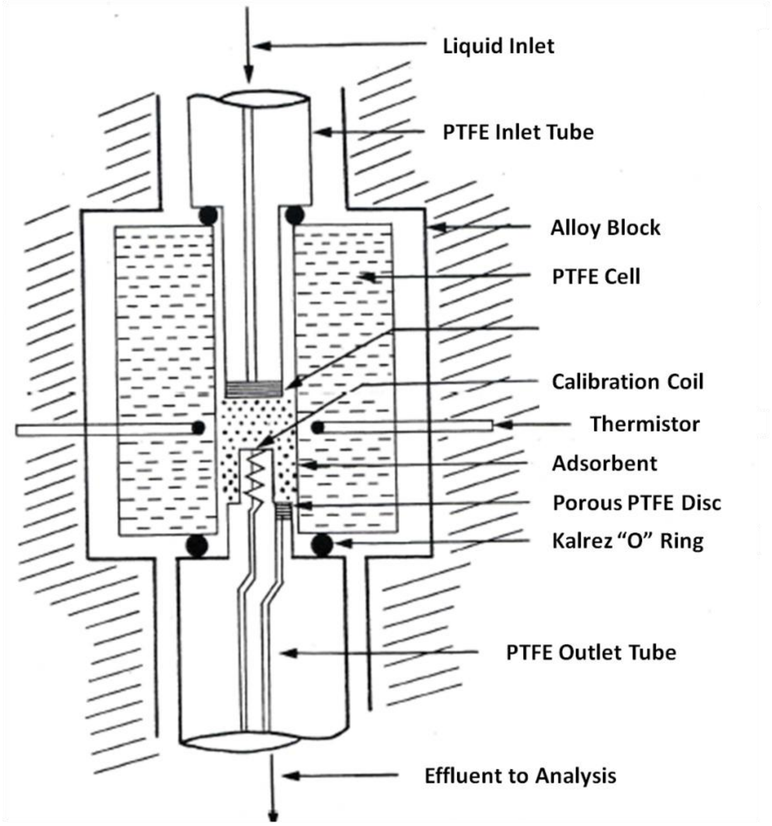

Figure 1-2 Diagram of the thermodynamic cell for a Mark 4V of the Microscal Flow Microcalorimetry. The schematic was adapted from the Microscal FMC manual.

In this study we explore the enthalpy of adsorption from solution onto graphite for a series of aliphatic adsorbates. The series of adsorbates varies based upon the terminal functional group (methyl, alcohol, thiol, bromo, and carboxylic acid). The monolayer structure for each adsorbent is already known from the STM literature. By comparing the experimental enthalpies of adsorption for this series to computationally derived lattice energies for the known monolayer structures (Figure 1-3) we can provide a benchmark for computational work with implications for selective adsorption at the solution/solid interface. Details of this study are available in chapter 3.

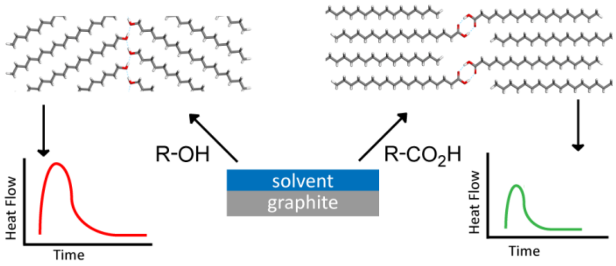

Figure 1-3 Monolayer structures for various aliphatic adsorbents are used to compare computationally derived lattice energies and experimental enthalpies of adsorption from solution.

Active Learning Strategies in the College Classroom

The most common model of teaching at the university level is "teaching as telling" where the primary job of the instructor is to convey the information that the students need to know.[41] Research shows that students do not learn (well) when instructors do all the work of constructing and conveying ideas,[42–45] especially when the learning goals extend beyond regurgitation of information[46] to critical thinking, problem solving, and transfer.[47] Huston provides an engaging, research-based example of how to get started creating an active learning environment in *Teaching What You Don't Know.*[48]

In contrast to the above model of teaching as transmission is a learner-focused model called constructivism.[49,50] In constructivism, the student's role is to engage the content and the teacher's role becomes facilitating student engagement.[51] In the educational literature, one set of strategies for facilitating student learning are called active learning strategies.[42,45] While there is an existing professional development literature on teacher training,[52–60] little is known about how active learning strategies are learned by the teachers. To exploring this void in the literature an active learning professional development program was designed to work within the existing context of the general chemistry lecture (CHEM 130) discussion sections to introduce active learning strategies to the GSIs. As design-based research,[61–63] both the program and the program goals were studied. Through qualitative research methods[64,65] the GSIs "image" of active learning and how they integrated these images it into their discussion sections were explored. Relevant to future iterations of the program was to also understand what portions of the professional development design had perceived benefit to the GSIs in their teaching practice. Details of the program and findings for the current iteration are developed in chapter 4.

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Chapter 2

Two-Dimensional Crystals from Reduced Symmetry Analogues of Trimesic Acid

Introduction

Long-range order in a layer of molecules assembled on a substrate can result in a two-dimensional (2D) crystal. In such 2D crystals, favorable molecule-molecule and molecule-substrate interactions can be incorporated at the stage of molecular design to promote long-range order during self-assembly.[1,2] The number and type of available inter- and intramolecular interactions available influence the pattern of the 2D crystal. As compared to three-dimensional (3D) crystals, this reduced dimensionality limits the number of ways to describe symmetry from 230 space groups in 3D to 17 plane groups in 2D. Molecules that engage in directionally defined interactions are ideal for the formation of precisely ordered porous structures in the bulk or on surfaces.

Trimesic acid (1,3,5-benzenetricarboxylic acid, **TMA**) is an archetypal, rigid, highly symmetrical molecule offering three hydrogen bonding moieties directionally favorable for the formation of ordered, nanoscale porous networks. The 2D self-assembly of **TMA** has been extensively studied in the literature at the solution/highly ordered pyrolytic graphite (HOPG) interface by scanning tunneling microscopy (STM).[3–12] This study focuses on 2D crystals formed from analogues of **TMA** where molecular symmetry is reduced within the series by the addition of one or more phenylene spacers (Figure 2-1). This strategy for reducing molecular symmetry is expected to reduce the symmetry of the resultant 2D crystal due to the loss of two and/or threefold symmetry within the series. This approach to reducing molecular symmetry has met with success in 3D crystal engineering of coordination polymers where the resultant reduction of network symmetry thwarts interpenetration.[13] Therefore the manifestation of symmetry reduction in controlling 2D assembly is of particular interest as a complexity-generating operation. During the structural investigation of various assemblies of the reduced symmetry analogues of TMA, six different phases were observed in four different plane groups, including a disordered assembly. Similarities in the segregation of the substituted carboxylic acids in the cyclic hydrogen bonded dimers in 2D and carboxylates in related 3D coordination polymers is observed.

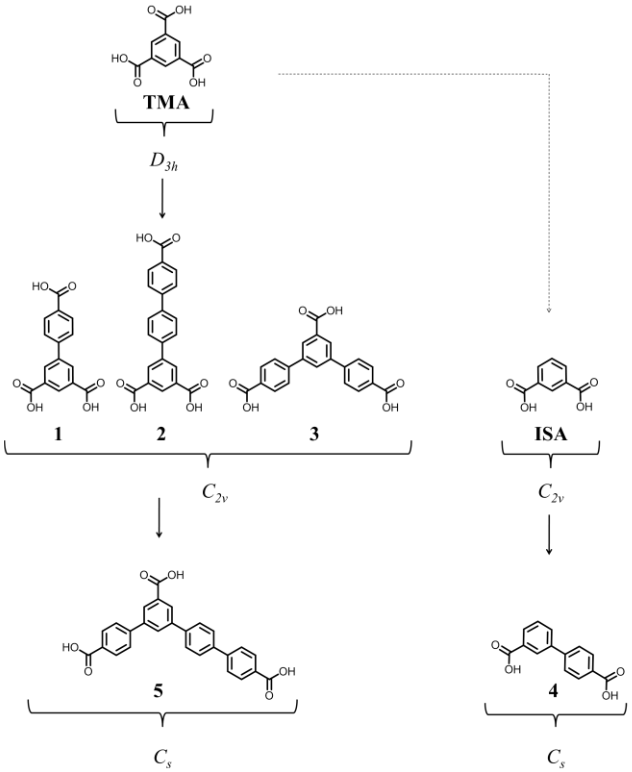

Figure 2-1 Molecular structures for the molecules investigated in this study. The dashed line represents a reduction in symmetry within the series by varying the number of carboxylic acid groups. The assigned point group symmetries treat carboxylic acids as carboxylates to be consistent with the resolution achievable in the STM images.

Experimental

Materials

1[14], **3**[15]**,** and **4**[16] were synthesized according to literature methods. Heptanoic acid (98%) was purchased from Acros. Molecule **2** was synthesized by Jennifer K. Schnobrich. Molecule **5** was synthesized by Ananya N. Dutta.

Scanning Tunneling Microscopy

A Nanoscope E STM (Digital Instruments) was used for all imaging. Highly oriented pyrolytic graphite (HOPG) (SPI-1 grade, Structure Probe Inc.) was used as a substrate for monolayer formation. A heptanoic acid solution of the desired molecule was made, of which 2 μL was placed on freshly cleaved HOPG to obtain a self-assembled monolayer. Each solution was at or near saturation in heptanoic acid. STM tips were made from Pt/Ir (20% Ir, 0.010 inch diameter, California Fine Wire) by mechanical cutting. Imaging was performed under ambient conditions and typical STM settings consist of 300 pA current and 700-900 mV bias voltage (sample positive). All images are unfiltered. For a specific image, the cell constants may vary from the average due to the drift of the STM tip. Cell constants and symmetries were determined by examining several images of both scan directions to account for this phenomenon.

Computational Modeling

Molecular mechanics modeling of the two-dimensional assemblies was performed in Materials Studio version 4.3 (Accelrys Software Inc.) using the assembled patterns and symmetry resolved in STM images (solvent omitted). Each lattice was geometry optimized in the Forcite module using the COMPASS force field[17] without molecule or lattice constraints. This method has been shown to correctly describe the geometry and relative energy stability of 3D polymorphic arrangements in molecular crystals.[18] Models of each lattice were built such that a layer of the model in the *ab* plane represents the arrangement of molecules observed in the STM images for a given phase. The *c*-axis, which is the distance between monolayers, was set to 100 Å for all models to minimize intermolecular interactions out of the *ab* plane and this axis changed less than 3 Å during optimization.

Results and Discussion

Molecular Design Strategy

The molecular design strategy employed in this study involves the asymmetrical addition of a phenylene spacer between the central benzene ring and one or more carboxylic acid of **TMA** or isophthalic acid. Isophthalic acid (1,3-benzenedicarboxylic acid, **ISA**) is a reduced symmetry analogue of **TMA**, due to the decrease in number of carboxylic acids from three to two. The first two asymmetrical variations in the structure of **TMA** are made by the addition of phenylene spacers in one direction, thus reducing the point group symmetry from ~D_{3h} to ~C_{2v}. The assigned point group symmetries throughout this work treat carboxylic acids as carboxylates to be consistent with the resolution achievable in the STM images. The biphenyl analogue of **TMA** (**1**) and the terphenyl analogue (**2**) (Figure 2-1) both have a 1:2 ratio of symmetry inequivalent carboxylic acids. If two phenylene rings are added between the central aromatic ring and two carboxylic acid moieties of **TMA**, then molecule **3** is obtained which, like **1**, **2**, and **ISA**, displays ~C_{2v} symmetry. Molecule **3** also has a 1:2 ratio of symmetry inequivalent carboxylic acids. The molecular symmetry of **ISA** is reduced to ~C_s by the insertion of a single phenylene ring between one carboxylic acid and the core benzene ring (**4**). Molecule **4** has a 1:1 ratio of symmetry inequivalent carboxylic acids. If a second phenylene spacer is added to molecule **3** between the central meta-substituted benzoic acid and one of the para-substituted benzoic acids, molecule **5** is derived. Molecule **5** has ~C_s symmetry and a 1:1:1 ratio of symmetry inequivalent carboxylic acids. Using STM, the pattern of the self-assembled monolayer(s) that each molecule forms at the solution/HOPG interface is examined. The relationship between the point group of each molecule with respect to the symmetry of the assembled network(s) will be discussed for each monolayer phase. In some cases more than one phase was observed and therefore each is discussed separately.

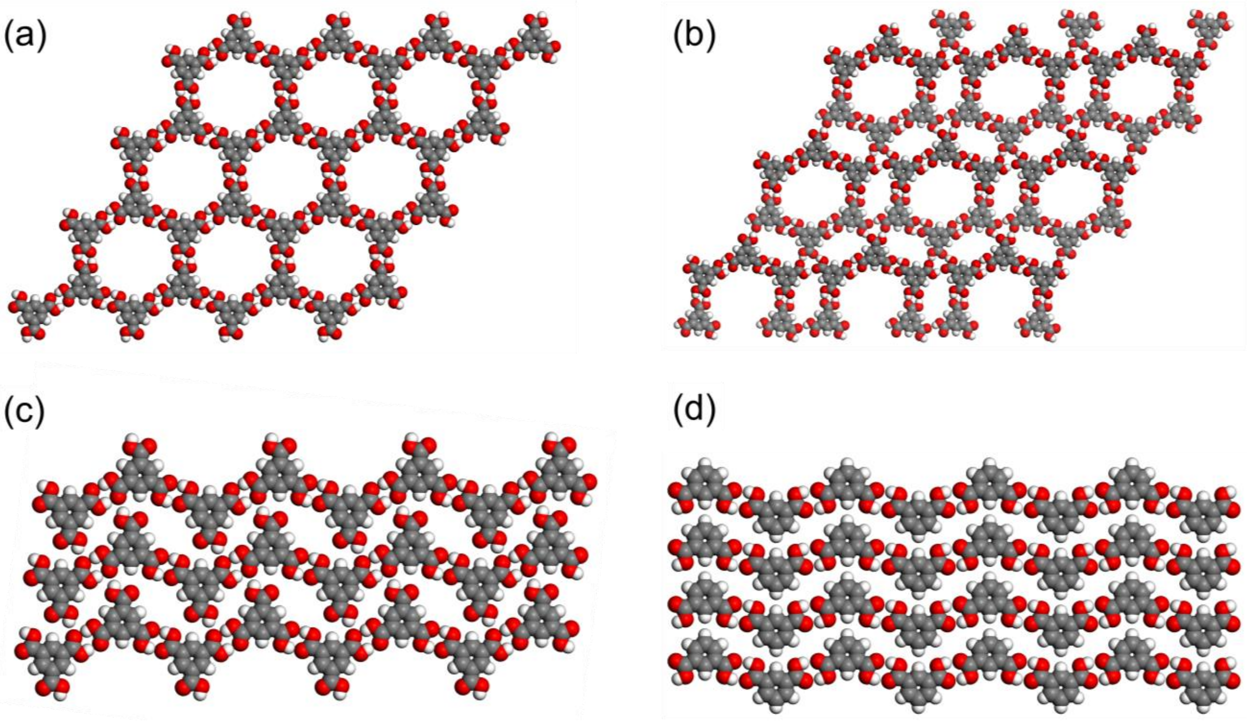

Figure 2-2 Computed models of (a) the chicken wire phase of TMA,[4,5] (b) the flower phase of TMA,[4,5] (c) the close packing phase of TMA,[12] and (d) ISA 2D crystals[19] based on literature STM studies at the solution/HOPG interface.

2D Crystals of ***TMA*** *and* ***ISA***

The 2D crystals of **TMA** and **ISA** have been investigated in the literature at solution/HOPG interfaces. Computed models of the known phases for each molecule are shown in Figure 2-2. The “chicken wire” phase is a planar array of fused hexagons with a **TMA** molecule at each vertex. The hexagonal pores are ~1 nm in diameter and have been shown to accommodate guest molecules.[19–21] The chicken wire phase incorporates only hydrogen bonded dimers of **TMA**. The flower phase resembles the chicken wire phase in that it has hexagonal pores with a **TMA** molecule at each vertex, but in the flower phase these hexagons are not fused together. Instead, they are slightly offset such that a hydrogen bond trimer is formed at each of the corners of the hexagon with **TMA** molecules from two other hexagon vertices. This hydrogen bonded trimer forms a threefold axis of rotation. A small pore is present between the edges of adjacent hexagons in the flower phase. Both the chicken wire and flower phases are in the *p*6 plane group. A threefold axis of rotation lies on each **TMA** molecule in the chicken wire phase. However, in the flower phase, the threefold axis of rotation lies on the hydrogen bonded trimer, not on the **TMA** molecules themselves. A close packing phase of **TMA** has been demonstrated in dilute, solvophobic conditions.[12] This phase forms with zig-zag lines of **TMA** molecules held together by hydrogen bonds between the third carboxylic acid and the side of the dimers forming the zig-zag lines. This close packing phase is in the *p*2 plane group. Due to the unique hydrogen bond motif in the close packing phase, there are no threefold axes of rotation in that phase. **ISA** has one known phase: close packed ribbons of dimerized **ISA** molecules.[22] This 2D crystal is in the *p*2*gg* plane group. Structural features in the 2D crystals of the reduced symmetry analytes **1**-**5** will be discussed in the context of the known phases of **TMA** and **ISA**.

*Molecule **1***

Phase I. Molecule **1** forms a phase consisting of columns of hydrogen bonded meta-meta dimers, shown in Figure 2-3. Due to the two-fold symmetry from the hydrogen bonding of meta-meta dimers the apparent symmetry of this monolayer is *p*2. Plane group *p*2 is chiral, and the other enantiomer of this crystal is observed in separate domains; one such example is shown in

Figure 2-3c. Only homo-dimers are observed in the crystal. In other words, no cyclic hydrogen bonds are formed between meta- and para-substituted carboxylic acid moieties in this phase. The columns formed by dimers of **1** are separated by 5.79 ± 0.47 Å, a space too wide to allow for even weak hydrogen bonding between the columns. Using nonanoic acid as solvent, a longer alkyl fatty acid chain, the space between the columns of dimers increases (Figure 2-3c) suggesting a role for solvent inclusion between the columns of **1**.[23,24]

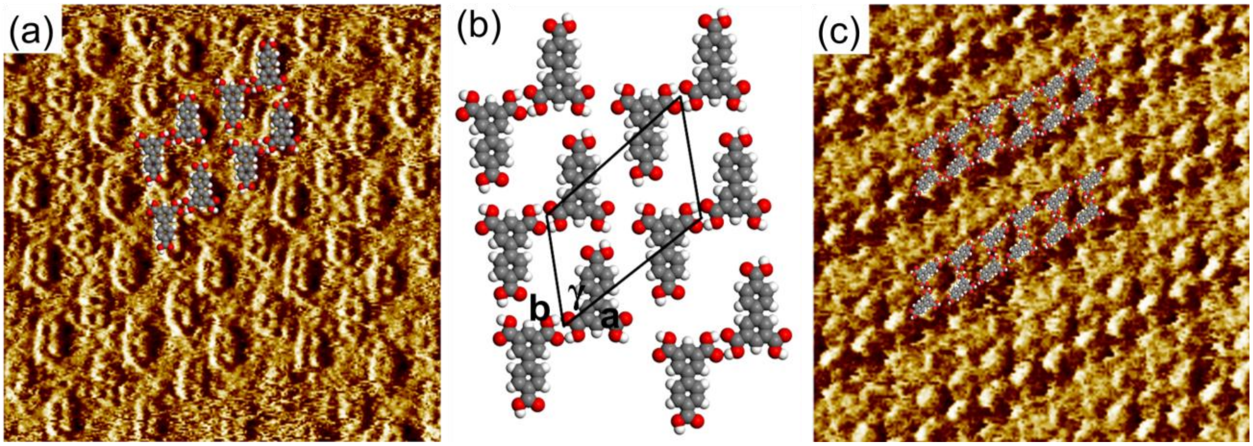

Figure 2-3 (a) STM image (10 × 10 nm^2) of Phase I formed by molecule 1 in n-heptanoic acid with overlaid molecular model, (b) computed model of the crystal structure of Phase I of 1, and (c) STM image (15 × 15 nm^2) of Phase I of 1 formed in n-nonanoic acid.

Phase II. Molecule **1** forms a zig-zag phase, shown in Figure 2-4, of repeating para-para and meta-meta hydrogen bond dimers. The "dangling" meta-substituted carboxylic acid is assumed to interact with the protic solvent in the space between the zig-zag rows, similar to Phase I. The length of the ribbon along the meta-meta dimer versus the para-para dimer results in an uneven herringbone-type pattern (Figure 2-4c). This 2D crystal has the apparent symmetry of *p*2, with the two-fold rotation axes at the center of each carboxylic acid homo-dimer. This phase is reminiscent of the ribbon phase of **ISA** (Figure 2-2d) but in this case the ribbons are slightly offset (γ = 83.5 ± 4.27°) and the width of the ribbon along each homo dimer differ.

While both Phase I and II of molecule **1** incorporate only homo dimers, Phase I is built from meta-meta dimers and Phase II ribbons is composed of both meta-meta and para-para homo dimers. Both phases are in the plane group *p*2, but in Phase I four of the nine two-fold rotation axes lie on the homo dimers and six of the nine two-fold rotation axes lie on the homo dimers in Phase II. While the motifs differ in local arrangement, column of dimers (Phase I) versus ribbons (Phase II), both phases incorporate only one unique molecule (*Z*' = 1).

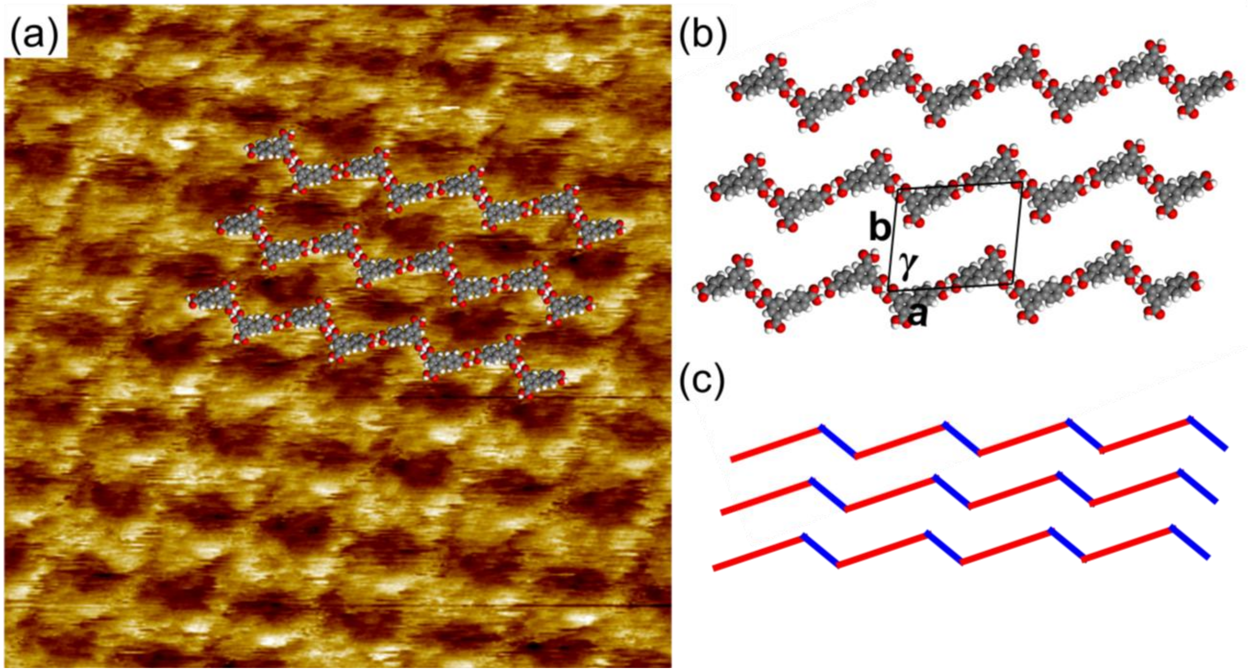

Figure 2-4 (a) STM images (15 × 15 nm^2) of Phase II of molecule 1 formed in heptanoic acid, (b) computed model of the crystal structure of zig-zag pattern, and (c) cartoon of the zig-zag phase highlighting the imperfect herringbone pattern.

The carboxylate analogue of the biphenyl tritopic linker, **1**, has been used to direct microporous coordination polymer (MCP) architecture. It is the organic linker in the material UMCM-150, the first material used to demonstrate reduced symmetry linkers as a route to preventing interpenetration in crystalline porous materials.[15] In UMCM-150, the two symmetry inequivalent carboxylates segregate at the metal nodes: the isophthalate carboxylates form copper paddlewheels and the para-benzoates form an unusual copper cluster $Cu_3(O_2CR)_6$. The 1:2 ratio of symmetry inequivalent carboxylates requires more than one type of copper cluster to be present in a given structure.[13] In contrast, **TMA** has only symmetry equivalent carboxylates and HKUST-1, the MCP which incorporates the carboxylate version of **TMA** as the organic linker, has only one kind of copper cluster.[25] The consequence of the statistical requirement in UMCM-150 is that there are two kinds of copper clusters and the carboxylates segregate between them within the structure. In 2D assembly, and without the presence of a metal center, if all carboxylic acids are dimerized it is not possible to have a single mode of association for **1** because of the stoichiometric imbalance of para and meta substitutions. In fact, carboxylic acid segregation is present and all **1**-**1** interactions are homo dimers: meta-meta or para-para.

Molecule **2**

The para-terphenyl derived tritopic linker, **2**, forms a phase with small pores as shown in Figure 2-5. The motif is formed by chains of repeating meta-meta dimers where the para-substituted carboxylic acids point in alternating directions along the *b*-axis of the crystal. The para-substituted carboxylic acids form homo-dimers linking the chains of meta-meta dimers and completing the elongated hexagonal pores (2.85×1.24 nm^2). This porous phase is an extended version of the chicken wire phase of **TMA** (Figure 2-2a). According to the molecular design strategy, molecule **2** is obtained when two phenylene rings are added between the phenylene ring and the same carboxylic acid of **TMA**. The added phenylene rings align with the *b*-axis in the crystal thus distorting the hexagonal chicken wire pores. With the loss of the three-fold symmetry as compared to **TMA**, the monolayer also loses three-fold symmetry features and lies in the rectangular plane group *cm*. Molecule **2** has not been shown to form a MCP, and as such no comparisons can be drawn between 2D monolayer and 3D behavior.

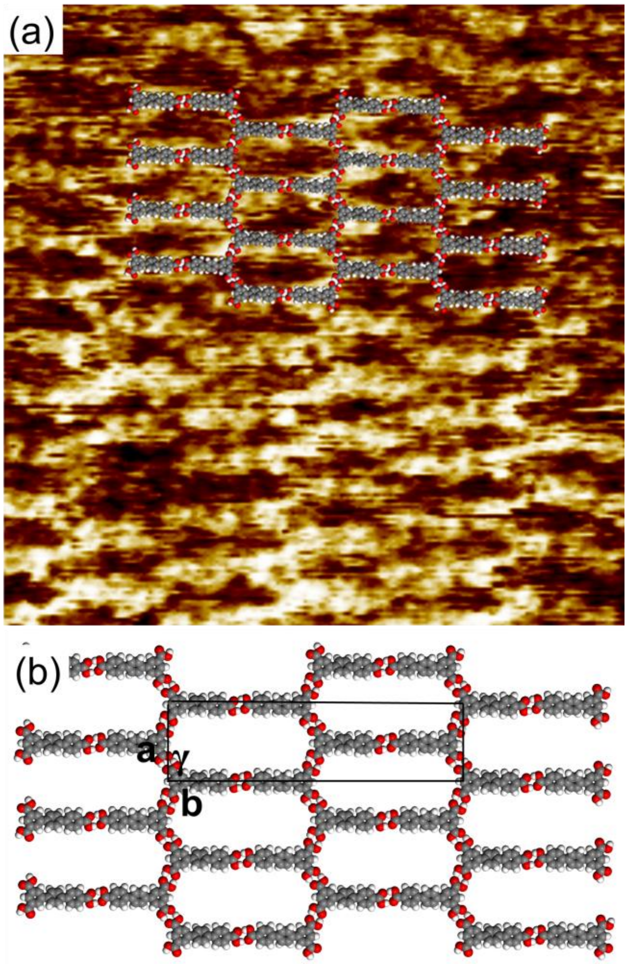

Figure 2-5 (a) STM image (20 × 20 nm^2) of the monolayer of molecule 2 with overlaid model and (b) the computed model of 2D crystal structure of molecule 2.

Molecule ***3***

The meta-terphenyl tritopic linker, **3**, forms a ribbon phase, shown in Figure 2-6. The **3**-**3** hydrogen bond dimers are composed of *trans*-para-para cyclic dimers. In these homo dimers, the two para-substituted carboxylic acid not involved in the dimer "point" in opposite directions on either side of the dimer. This phase is similar to that of **ISA** (Figure 2-2d) in that both have a 120° angle between the *trans*-homo dimers along a given ribbon. Unlike Phase II of molecule **1**, the width of the ribbon along the molecular axis for each homo dimer is consistent. The apparent symmetry of this 2D crystal is *p*2*mg*, a very uncommon plane group according to the 2D

Structural Database;[1] there are only two other compounds in the database that have monolayers with *p*2*mg* symmetry.[26–28]

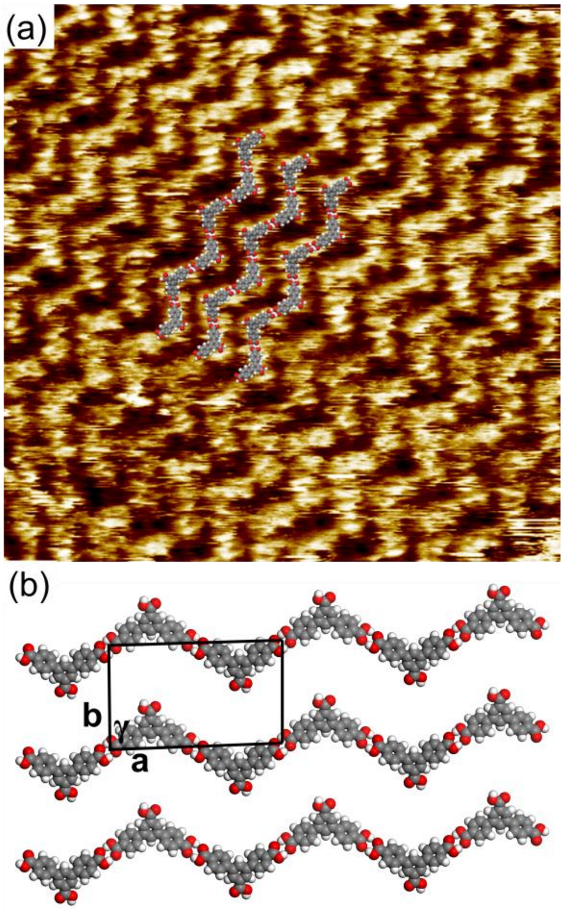

Figure 2-6 (a) STM image (30 × 30 nm^2) of the monolayer of molecule 3 with overlaid model and (b) the computed model of 2D crystal structure of molecule 3.

The carboxylate form of molecule **3** has been incorporated into the MCP UMCM-151, where the symmetry inequivalent carboxylates segregate such that each copper paddlewheel is coordinated by only para- or meta-substituted carboxylates.[13] To satisfy stoichiometry, there are two times as many para-coordinated paddlewheels as there are meta-coordinated paddlewheels. Similar to molecule **1**, in the case of **3** the 1:2 ratio of symmetry inequivalent carboxylates requires more than one kind of paddlewheel coordination in the MCP structure.

Molecule ***4***

The phase formed by molecule **4** is a ribbon structure exclusively incorporating hetero dimers (Figure 2-7). With the meta-para hydrogen bonds, the lack of two-fold rotation axes, and an offset alignment of neighboring ribbons the 2D crystal is in the plane group *p*1. This motif is built from two unique molecules (Z'=2) and as such is the only ordered phase in the series to incorporate more than one building block.

The carboxylate version of molecule **4** has been used as the organic linker in two isomeric MCPs.[16] Both isomers are comprised of copper paddlewheels of two meta- and two para-carboxylates, and vary in the arrangement of the carboxylates around the paddlewheel. In one structure the carboxylate substitutions alternate meta-para-meta-para around the copper paddlewheel and in the other structure the sequence of carboxylate substitution around the paddle wheel is meta-meta-para-para). The lack of carboxylate segregation is possible due to the 1:1 ratio of symmetry inequivalent carboxylates in **4**. More than one kind of paddlewheel is not required in a given structure to satisfy the stoichiometry of the carboxylates. The 1:1 ratio of symmetry inequivalent moieties in **4** results in mixed copper paddlewheels in 3D and hetero dimers in 2D.

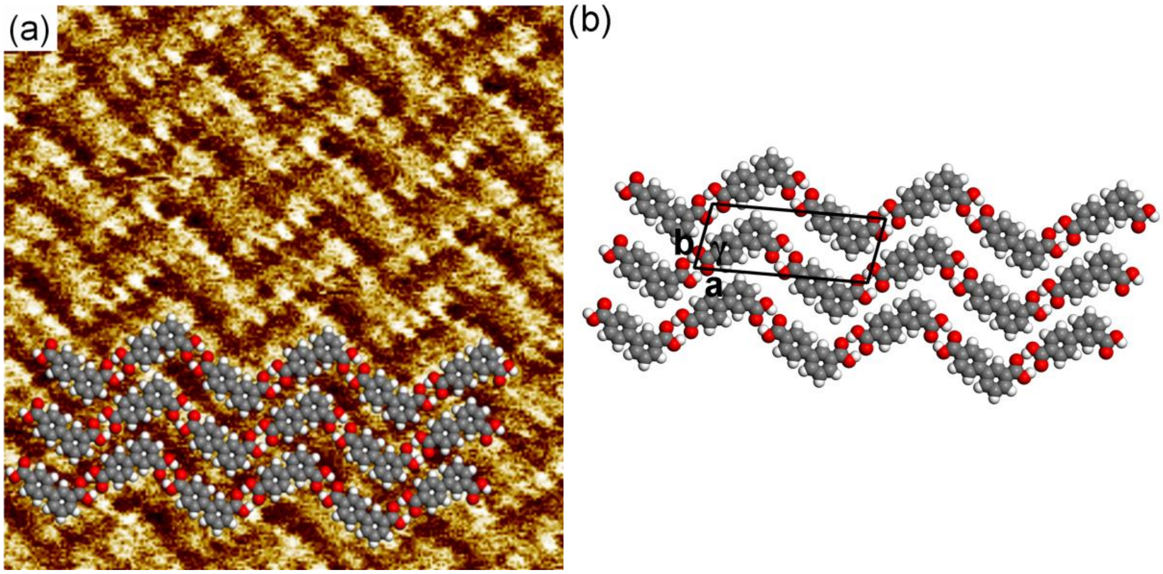

Figure 2-7 (a) STM image (10 × 10 nm^2) of the monolayer of molecule 4 with overlaid model and (b) the computed model of 2D crystal structure of molecule 4.

Molecule ***5***

The tritopic quaterphenyl linker, **5**, has three symmetry inequivalent carboxylic acids. The primary monolayer motif formed by **5** has no regular, repeating pattern (Figure 2-8). In contrast to the examples of large scale disorder[29–32] in the Two-Dimensional Structural Database (2DSD),[1] this assembly does not show areas of local order. Thermal annealing, dilution, and solvophobic conditions have been used in pursuit of obtaining an ordered phase for **5** and have thus far been unsuccessful. The three carboxylic acids are symmetry inequivalent, resulting in 12 unique dimers that could be formed by molecule **5** in 2D. The availability of so many competing arrangements may contribute to the formation of the disorder[33] at the solution/HOPG interface. Molecule **5** has not been shown to form a MCP, and as such no comparisons can be drawn between 2D monolayer and 3D behavior.

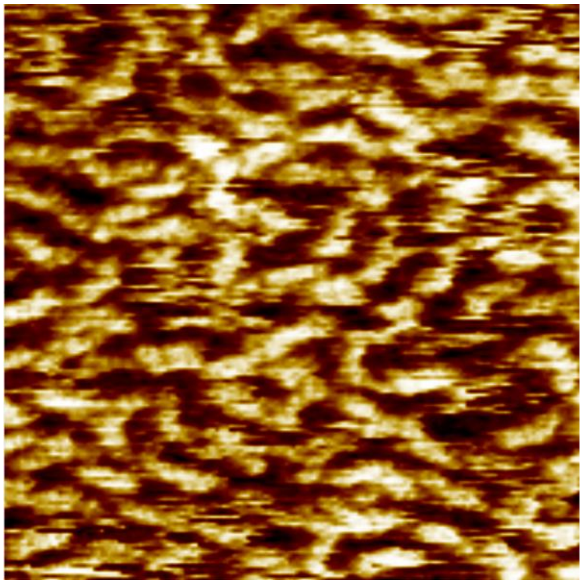

Figure 2-8 STM image (25 × 25 nm^2) of the monolayer of molecule 5 exhibiting disorder.

Table 2-1 Summary of relevant crystallographic information pertaining to the molecules of interest and the two-dimensional crystals formed.

Name	**Point Group**[a]	**Hydrogen Bonding Interaction**	**Plane Group**	**Z'**
TMA	D_{3h}	homo dimer	*p*6	1/3
		homo & hetero dimer	*p*6	1
		homo dimer & side	*p*2	1
1	C_{2v}	homo dimer	*p*2	1
		homo dimer	*p*2	1
2	C_{2v}	homo dimer	*cm*	1
3	C_{2v}	homo dimer	*p*2*mg*	0.5
ISA	C_{2v}	homo dimer	*p*2*gg*	0.5
4	C_s	hetero dimer	*p*1	4
5	C_s	disorder	n.a.	n.a.

[a] point groups are assigned for deprotonated structures

Comparisons

The monolayers formed from the five reduced symmetry analogues of **TMA** and **ISA** examined in this study show a strong dependence on the symmetry of the hydrogen bonding dimer in determining the structure of the resulting 2D crystals. Table 2-1 summarizes the point group for each molecule and the plane group for each monolayer based on the apparent symmetry in the image. The threefold axis of rotation in the apparent monolayer symmetry in monolayers of **TMA** was lost in monolayers assembly from molecules in this design strategy. Only one monolayer in this series does not incorporate homomeric hydrogen bonding (**4**) and that monolayer lies in the plane group *p*1. Of the five ordered monolayers formed for this series, four different plane groups were observed. In contrast, the 2D crystals formed from analogues of 1,3,5-benzenetribenzoic acid (H_3BTB) reduced by varying the number and position of carboxylic acids all exhibited *p*2 symmetry.[34]

From a molecular design perspective, **TMA** and **ISA** are the higher symmetry molecules which were used as the starting points for this route to a series of reduced symmetry multicarboxylated arenes through the addition of phenylene spacers (Figure 2-1). Both **TMA** and **ISA** have only symmetry equivalent carboxyl groups. As described above, cyclic hydrogen bonding plays an important role in the 2D structures of **TMA** (Figure 2-2a-c). In addition to the cyclic hydrogen bonded dimers in all three phases one third of the hydrogen bonds in the flower phase of **TMA** (Figure 2-2b) are cyclic hydrogen bonded trimers. The close packing phase of **TMA** (Figure 2-2c) incorporates a side hydrogen bond, but this phase is formed under unusual experimental conditions.[12]

For this series (Table 2-1), where there are only homo-dimers in 2D (molecules **1**, **2**, and **3**), any symmetry inequivalent carboxylates are phase segregated in the 3D MCPs such that only one kind of carboxylate symmetry is present at each metal-cluster. In the case of **4**, where hetero dimers are formed in 2D, the metal centers in the MCPs have a mixture of substituted carboxylates. There are no monolayers in this series with mixed hetero and homo dimers. In contrast, for a tetracarboxylate derivative of H_3BTB (5'-(4-carboxyphenyl)-[1,1':3',1"-terphenyl]-3,4",5-tricarboxylic acid), both homo and hetero dimers are formed in 2D[34] and the substitution of the carboxylates at each metal center in the two MPCs are mixed.[13] This is not surprising in light of different geometry requirements to fill space in 2D and 3D.

Conclusions

We have designed a series of five analytes related to **TMA**, an archetypal high symmetry adsorbate, through the addition of phenylene spacers. In contrast to monolayers formed from alternate routes to reduced symmetry adsorbates, self-assembly of molecules in this series yielded six monolayers in four different plane groups. The composition of the cyclic carboxylic dimers (homo or hetero dimers) in the resultant 2D crystals at the liquid/HOPG interface is related to the stoichiometric ratio of symmetry inequivalent carboxylic acids of each analyte. Additionally, the analyte with a 1:1:1 ratio of symmetry inequivalent carboxylic acids (**5**) formed a disorderd phase at the solution/HOPG interface. The composition of the dimers in 2D (homo or hetero) mirrors the carboxylates composition (meta- or para-substituted) at the metal centers in MCPs incorporating these carboxylated arenes as the organic linkers. Such findings have design implications for using molecular symmetry to guide complex assemblies in both 2D and 3D.

Future Directions

The two design-strategies for reducing symmetry within series' of multicarboxylated arenes are to varying either the position and/or number of carboxylic acids or to use phenylene spacers to break two- or three-fold axes.[13] Both strategies have now been examined for single-component two-dimensional self-assembly at the liquid/solid interface. Each route has generated different kinds of monolayer complexity at the liquid/solid interface. Studying adsorption from mixed solutions of molecules across this series will enable a better understanding of monolayer format. Two main behaviors may be expected from mixing two or more components: phase segregation of the individual components or coadsorption of different components. This may afford additional insight into factors contributing to two-dimensional network topology in increasingly complex systems.

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Chapter 3

Functional Group Effects on the Enthalpy of Adsorption for Self-Assembly at the Solution/Graphite Interface

Introduction

Early studies into the thermodynamics of monolayer self-assembly were conducted using mixing calorimetry.[1] Such work provided initial evidence that n-alkanes, in particular those that are liquid and near their melting point at room temperature, assemble in the presence of a substrate into a close packed arrangement maximizing substrate-adsorbate interactions by arranging the molecular long axis parallel to the substrate. Heats of adsorption for these alkanes suggested the formation of a monolayer[2] and this conjecture was later corroborated by neutron diffraction,[3] adsorption isotherms,[4] and scanning tunneling microscopy (STM).[5] STM has evolved into a robust tool to study the spatial and temporal components of monolayer self-assembly.[6–10] STM has also been used to investigate the thermodynamics of molecular assembly; from a mixed-analyte solution the difference in free energy between the phase-segregated assemblies can be calculated.[11,12] These relative free energy values can quantify the driving force for preferential assembly from a given mixed-analyte solution. Extrapolating these free energies outside the specific analyte/solvent/substrate system examined is not generally possible, and thus the thermodynamic insight into monolayer formation available from STM images is limited. Moreover, comparison to computational methods, which excel at computing enthalpies of assembly rather than free energies, leads to a disconnect between experiment and theory.

The energies of intermolecular interactions in ordered monolayers are often approximated by lattice energies calculated using molecular mechanics (MM).[7,13–19] MM can be used to deconvolute the relative contributions of intermolecular interactions within a monolayer; however, physisorption and order within monolayers at the solution/solid interface also depend on analyte-substrate, substrate-solvent, and analyte-solvent interactions. While these additional interactions can be modeled and more sophisticated techniques and hybrid approaches[20–23] have increasingly been applied, approximations are inherent and there is a paucity of thermodynamic data available for benchmarking. Here we quantify the thermodynamics of self-assembly at the liquid/solid interface with flow microcalorimetry (FMC) experiments encompassing all analyte, solvent, and substrate interactions simultaneously and contrast these experimental values with computationally derived lattice energies. This study works to bridge the information gaps of STM and MM to understand the limits of using energy of a modeled lattice to approximate the enthalpy of adsorption of an ordered, physisorbed monolayer. The ultimate goal is to achieve a more complete understanding of the thermodynamics of self-assembly at the liquid/solid interface: an issue of critical importance in understanding selective adsorption from complex mixtures of the sort critical for industrial separations. Moreover inasmuch as graphite is a model for certain carbonaceous sorbents, such data inform, at a molecular level, the thermodynamics of adsorption onto an important sorbent class. Experimental enthalpies of adsorption from solution for a series of aliphatic molecules, the stearyl series (Figure 3-1), are reported herein and are discussed in the context of lattice energies from MM and monolayer patterns from the STM literature.

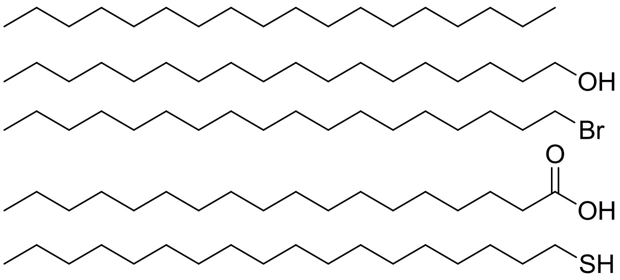

Figure 3-1 Structures of five molecules examined here as the stearyl series.

Experimental

Materials

Octadecane (99+%), 1-bromooctadecane (96%), and 1-octadecanethiol (96%) were purchased from Acros. 1-Octadecanol (≥99.0%) and stearic acid (99+%) were purchased from Aldrich. The solvent, HPLC grade n-heptane, was purchased from Fisher.

Powdered graphite, 1-2 micron, was purchase from Aldrich. A sample was heated on a TA Instruments Q50 thermogravimetric analyzer to 600 °C at a rate of 10 °C/min. There was 0.842 % loss after 282 °C. To remove adsorbates from the graphite, a bulk sample was heated in a tube furnace at 300 °C for 12 hours under vacuum. After activation the tube was back filled with nitrogen gas, and the activated graphite was stored in a glovebox under a nitrogen atmosphere; small portions were removed as necessary for use in flow microcalorimetry experiments.

Nitrogen Sorption

N_2 sorption was carried out on a Quantachrome Autosorb 1 using 99.999% purity N_2 (Cryogenic Gases). Activated, powdered graphite (~200 mg) was transferred to a sample cell in a N_2 glovebox and attached to the surface area analyzer. Samples were immediately subjected to dynamic vacuum, after which surface area analysis was performed.

Scanning Electron Microscopy

Dry powdered graphite samples were dispersed onto conductive carbon tape. SEM was performed using a Nova Nanolab Dualbeam FIB-SEM operated at 5 kV equipped with a Schottky field emission gun (FEG) electron source and an in-lens secondary electron detector.

Flow Microcalorimetry

A Mark 4V flow microcalorimeter (FMC) manufactured by Microscal LTD was used for all calorimetry. The essential instrument details have been described elsewhere.[24] A figure of the thermodynamic cell is available in chapter 1. Approximately 25 mg activated, powdered graphite was placed in the cell. To settle the adsorbent, the cell was tapped for approximately 30 seconds after the graphite was placed inside. The solvent, n-heptane, was introduced into the calorimeter with sequentially decreasing flow rates: 60, 30, 15, 9, and 3 mL/hr for five minutes at each rate. After the adsorbent was wetted with solvent it was allowed to thermally equilibrate over several hours at a flow rate of 3 mL/hr. Stability was indicated by a constant calorimeter heat flow reading. The flow rate during the adsorption experiment was kept at 3 mL/hr.

Each adsorption experiment involves a calibration event, where a known amount of energy is applied to the cell while solvent is flowed through the cell at 3 mL/hr. The measured response is integrated against the baseline, and this calibration value is used to quantify the thermal adsorption event. The Microscal calorimeter digital output and sequencing software (CalDOS) automatically records, calibrates, and integrates the thermodynamic data. For each experiment, a solution of one of the analytes in n-heptane at a known concentration was flowed through the cell (octadecane, 138-141 mM; 1-bromooctadecane 23.9-24.6 mM; 1-octadecanethiol, 35.2-70.0 mM; 1-octadecanol, 7.03-17.6 mM; stearic acid, 7.03-17.6 mM). The enthalpies of adsorption for different compounds plateau at different concentrations;[2,25] the experimental concentrations were chosen with consideration of the solubility of the component in n-heptane. Adsorption of the analyte onto the substrate when solution is flowed through the cell causes a change in the cell temperature, which is converted into a heat signal using a calibration factor. The effluent is allowed to flow until thermal equilibrium was established for each event. Each analyte was tested 3 to 5 times and an average experimental value is reported for each analyte with error corresponding to the standard deviation of the mean.

Molecular Modeling

Molecular mechanics modeling of the two-dimensional assemblies was performed in Materials Studio version 4.3 (Accelrys Inc.) using the assembly pattern and symmetry from STM images in the literature. Each lattice was geometry optimized in the Forcite module using the COMPASS force-field[26] without molecule or lattice constraints. The lattice parameters from the MM and STM literature show a high level of agreement (Table 3-1). Models of each lattice were built such that a layer of the model in the *ab* plane represents the arrangement of molecules observed in the STM literature. The *c*-axis, which is the distance between monolayers, was set to 100 Å for all models to minimize intermolecular interactions out of the *ab* plane, and changed less than 1 Å during geometry optimization. A single molecule of each analyte in a 100 × 100 × 100 $Å^3$ unit cell was modeled in the same manner to determine the energy of an “isolated” molecule. The COMPASS force-field has been shown to agree well with experimental enthalpy data for the relative stability of three-dimensional pharmaceutical polymorphs.[27] The energy of an isolated molecule was subtracted from the energy of a lattice for each molecule in the series to obtain a lattice energy.

Electronic Structure Calculation

Spartan '10[28] was used to investigate the theoretical enthalpy of solvation for one molecule in the fully extended, all-*trans* conformation for each analyte in the stearyl series. The equilibrium geometry was calculated in the ground state using the Hartree-Fock model and the 6-31G* basis set. Heptane was included as the solvent during the calculation using the SM8 model,[29] a continuum model of solvation. The reference state for the calculated solvent energies is the gas phase.

Table 3-1 Unit cell parameters

	from STM literature			from molecular modeling		
	a (nm)	b (nm)	γ (°)	a (nm)	b (nm)	γ (°)
1-octadecanol[30,31]	4.5	0.5	90	4.37	0.51	90.0
1-octadecanethiol[32]	8.7	not reported		9.31	0.51	90.0
stearic acid[33,34]	5.2	0.9	96	5.69	0.88	90.0
octadecane[35]	4.8	0.4	90	5.01	0.44	89.9
1-bromooctadecane	not reported			5.38	0.44	89.5

Results

The molecular structures for the stearyl series (Figure 3-1) incorporate five different terminal functional groups. Varying the terminal functional group allows access to different monolayer patterns while controlling for possible differences in adsorption strength due to the length of the alkyl chain.[36] The enthalpy of adsorption from solution onto powdered graphite for each analyte in the series was experimentally determined (Table 3-2); a lack of concentration dependence supports monolayer coverage.[37] Powdered graphite was chosen as the substrate to model highly ordered pyrolytic graphite (HOPG) in the experimental enthalpy of adsorption experiments because it retains the large basal planes for adsorption (Figure 3-4), but has a higher surface area than HOPG allowing for more precise determination of evolved heat upon adsorption. The pattern that each analyte makes in a monolayer upon assembly is modeled based on literature STM data focusing on assembly from solution not vapor[38] onto HOPG; details of the known monolayer patterns are discussed below. The unit cell dimensions from the known patterns allow the experimental enthalpy of adsorption on powdered graphite to be expressed not only per unit mass of adsorbent, but also as the enthalpy per mole of analyte adsorbed. The experimental enthalpy of adsorption data are thus of compatible units for comparison to computationally derived lattice energies (Table 3-3).

Table 3-2 Summary of experimental enthalpies of adsorption.

Analyte	**ΔH_s (kcal/g graphite)**	**Area per molecule[a] (nm^2/molecule)**	**ΔH_a (kcal/mol analyte)**
1-octadecanol	$-2.72 \times 10^{-4} \pm 1.75 \times 10^{-5}$	1.11	-16.8 ± 1.1
1-octadecanethiol	$-1.98 \times 10^{-4} \pm 9.39 \times 10^{-6}$	1.18	-13.0 ± 0.6
stearic acid	$-1.74 \times 10^{-4} \pm 6.99 \times 10^{-6}$	1.26	-12.2 ± 0.5
octadecane	$-1.32 \times 10^{-4} \pm 1.03 \times 10^{-5}$	1.11	-8.15 ± 0.63
1-bromooctadecane	$-1.07 \times 10^{-4} \pm 4.06 \times 10^{-6}$	1.19	-7.14 ± 0.27

[a] Area per molecule is derived from the modeled lattice constants in molecular models based upon the assembly shown in the STM image for each analyte. ΔH_s refers to the enthalpy of adsorption from solution per mass adsorbent. ΔH_a refers to the enthalpy of adsorption from solution per mole of analyte.

Enthalpy of Adsorption from Solution

The information captured by the flow calorimetry experiments encompasses the cumulative thermodynamics for all interactions during self-assembly at the liquid/solid interface:

solvent-solvent, solvent-substrate, analyte-solvent, analyte-analyte, and analyte-substrate. The analytes in the stearyl series all have a saturated alkane chain of seventeen carbons and vary only in their terminal functional group: methyl, bromo, thiol, alcohol, and carboxylic acid (Figure 3-1). All five analytes in this series have enthalpies of adsorption of the same sign and of similar magnitude consistent with an enthalpically favorable adsorption of the alkyl chain with higher order effects arising from the specific functional groups present. The least exothermic adsorption for the analytes in the stearyl series is that of 1-bromooctadecane followed closely by that of octadecane, at -1.07×10^{-4} and -1.32×10^{-4} kcal/gram graphite respectively (Table 3-2). The enthalpy of adsorption for stearic acid is -1.74×10^{-4} kcal/gram graphite, only 0.42 kcal/gram graphite more exothermic than that of octadecane. While the cyclic carboxylic acid hydrogen bond dimer is a robust and versatile hydrogen bonding synthon,[39] the inclusion of dimers in the monolayer structure does not result in the most exothermic adsorption from solution. The 1-octadecanethiol adsorption enthalpy, also greater than that of octadecane, is -1.98×10^{-4} kcal/gram graphite. The highest enthalpy of adsorption is that of 1-octadecanol at -2.72×10^{-4} kcal/gram graphite. Thus, variations in the terminal functional group for the stearyl series do result in distinct enthalpies of adsorption from solution. The relative ordering within the series will be discussed below in the context of monolayer structural features.

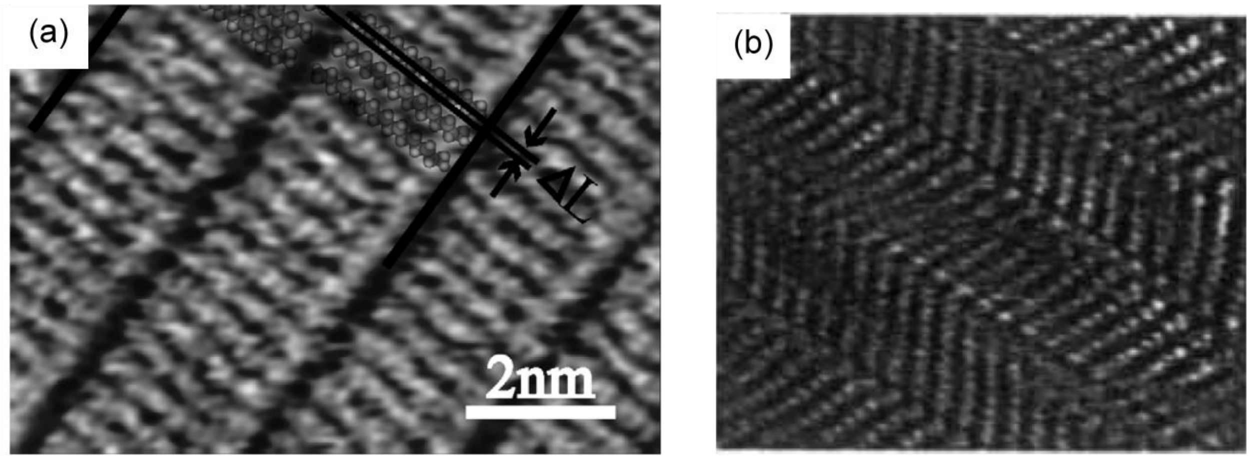

Figure 3-2 Representative STM images adapted from the literature for (a) a linear pattern of octadecane[35] at the neat alkane/HOPG interface and (b) a herringbone pattern formed by 1-octadecanol in phenyloctane at the solution/HOPG interface (image size 9.7 × 7.8 nm^2).[45]

The above analysis gives enthalpies of adsorption in terms of grams of adsorbent; however because monolayer densities can differ, the structure of a monolayer of each adsorbate must be known to probe the effect of the functional groups on the molar enthalpy of adsorption. STM is a powerful tool to reveal monolayer patterns at solution/solid interfaces. In the presence of HOPG, the molecules in the stearyl series assemble in the all-*trans* conformation parallel to the graphite substrate. The patterns observed by STM for the stearyl series on HOPG fall into two general motifs: linear and herringbone (Figure 3-2). The packing patterns for the two-dimensional crystals were extracted from the literature images and descriptions for each assembly were used to build the corresponding molecular models as shown in Figure 3-3. The linear patterns of octadecane[35] and 1-bromooctadecane[35,40] have well-defined columns of molecules oriented 90° to the column direction (Figure 3-3a and b respectively). The self-assembly of stearic acid also forms linear lamellae with fully extended cyclic hydrogen bonded dimers interdigitated perpendicular to the trough (Figure 3-3c).[33,34,41–43] Both 1-octadecanol[44–46] and 1-octadecanethiol[32] assemble in a herringbone pattern: individual molecules assemble head-to-head with the molecular axes tilted ~60° relative to the neighboring troughs.

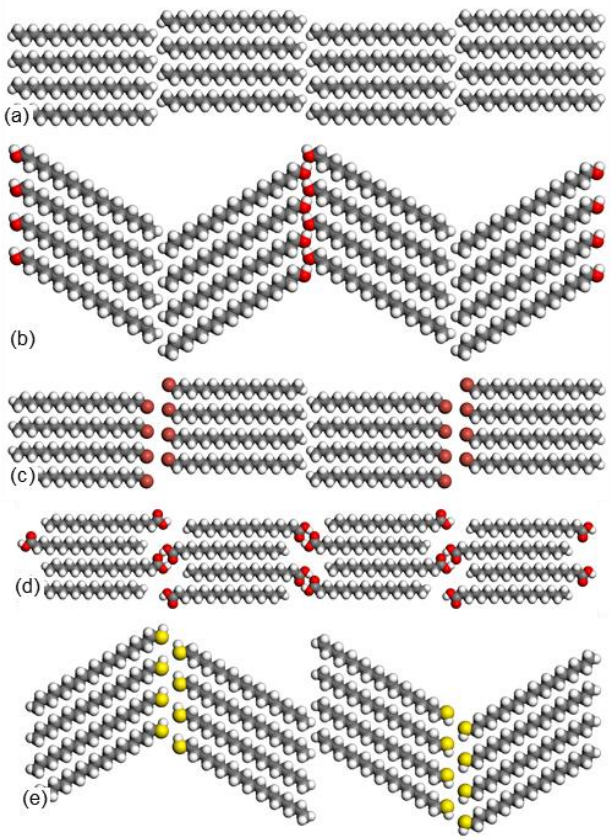

Figure 3-3 Molecular models of the packing patterns for monolayers of (a) octadecane,[35] (b) 1-octadecanol,[44–46] (c) 1-bromooctadecane,[35,40] (d) stearic acid,[33,34,41,42] and (e) 1-octadecanethiol[32] based on literature STM images. Atom colors correspond to carbon (grey), hydrogen (white), oxygen (red), bromine (brown), and sulfur (yellow).

A molecular model for a monolayer of each analyte was built. The area per molecule was calculated using unit cell dimensions and the number of molecules per unit cell (*Z*) from the models. The unit cell area per molecule ranges from 1.11 to 1.26 nm^2 for this series (Table 3-2). Using this information the enthalpy of adsorption relative to the amount of substrate, ΔH_s, can be expressed relative to a mole of adsorbed analyte, ΔH_a, using the following equation:

$$\Delta H_a = \Delta H_s \times \frac{unit\ cell\ area}{Z} \times \frac{N_A}{S}$$

where ΔH_s is the enthalpy of adsorption relative to the mass of substrate (kcal/gram graphite), *Z* is the number of molecules in the unit cell, S is the surface area of the adsorbent

(m^2/g adsorbent), and N_A is Avogadro's number. The BET surface area for the activated, powdered graphite (10.8 m^2/g) was calculated from the nitrogen sorption isotherm. The lack of significant porosity and prominence of the graphite basal planes is supported by SEM analysis of the graphite (Figure 3-4). This lack of significant porosity indicates that all of the BET accessible surface area can be assumed to available for monolayer formation. The prominence of basal planes supports the use of powdered graphite as a reasonable approximation for highly ordered pyrolytic graphic as the substrate. Adsorption on the edges of the graphite, which are included in the BET-determined surface area, is presumed to be a minor contributor to the overall heat of adsorption based on the particle morphology.

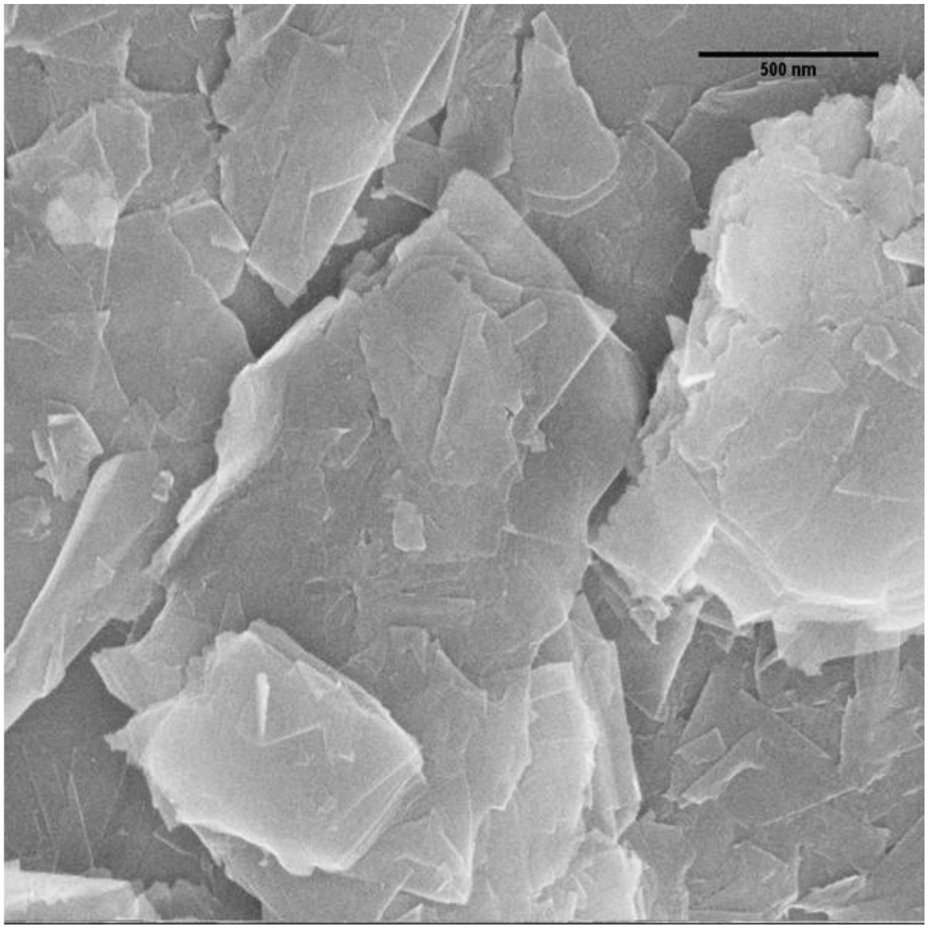

Figure 3-4 SEM micrograph of powdered graphite used as the sorbent during flow microcalorimetry experiments showing large basal planes for adsorption.

The experimental enthalpies of adsorption per mole of adsorbed analyte, ΔH_a, reflect the same ordering as the enthalpy of adsorption per gram of adsorbent, ΔH_s (Table 3-2). Again, the bromo and methyl terminated analytes give the least exothermic enthalpies of adsorption: -7.14 and -8.15 kcal/mol analyte, respectively. The carboxylic acid terminated analyte has the next most exothermic enthalpy of adsorption: -12.2 kcal/mol. The enthalpy of adsorption for the thiol terminated monolayer is -13.0 kcal/mol whereas the alcohol has the most exothermic enthalpy of adsorption (-16.8 kcal/mol). Both expressions for the experimental enthalpy of adsorption (ΔH_a and ΔH_s) have the same sign, magnitude, and ordering for the stearyl series.

Computationally Derived Lattice Energies

Molecular modeling allows quantitative assessment of the strength of intermolecular interactions. The analyte-analyte interactions revealed by STM for each monolayer in the stearyl series were modeled. Comparing the experimental adsorption from solution to the lattice energies (Table 3-3) shows that the modeling does not wholly reflect the same ordering of the monolayer assemblies given by the flow microcalorimetry experiments and, specifically, stearic acid and 1-bromooctadecane are the outliers. The calculated values for the 1-bromooctadecane and octadecane, -12.4 and -12.0 kcal/mol respectively, have the opposite ordering as the experimental enthalpies of adsorption but do reflect expected ordering for adsorption from the gas phase.[47] The modeling predicts that 1-octadecanethiol has the next largest lattice energy (-13.4 kcal/mol), followed by stearic acid (-17.0 kcal/mol), and finally 1-octadecanol (-19.6 kcal/mol). Thus MM ranks stearic acid as the second highest in the series, whereas in the experimental enthalpies of adsorption from solution it is ranked third highest. The calculated lattice energies are similar in sign and magnitude to the experimental enthalpies of adsorption from solution; while fortuitous this does not affirm the validity of lattice energies as a comprehensive model for the thermodynamics of adsorption from solution. The ordering of the analytes according to the computationally derived lattice energies differs from that given by the experimental enthalpies of adsorption from solution. To deconvolute this difference, the critical role of solution-phase interactions is discussed below.

Table 3-3 Lattice energies of the periodic models of the stearyl series computed in the COMPASS force-field (kcal/mol analyte)[a]

	lattice energy	**valence term**	**van der Waals term**	**electrostatic term**
1-octadecanol	-19.6	0.1	-10.7	-9.0
1-octadecanethiol	-13.4	-0.1	-12.9	-0.4
stearic acid	-17.0	-0.5	-9.0	-7.5
octadecane	-12.0	0.0	-12.0	0.0
1-bromooctadecane	-12.4	-0.1	-12.6	0.3

[a] These values represent the energy obtained by the formation of the periodic assembly from isolated single molecules.

Discussion

Enthalpies of adsorption from solution, lattice energies and related monolayer patterns have been considered thus far in this study. We now turn our attention to the connection of these values to the structures of the monolayers. From the calorimetry experiments, exothermic enthalpies of adsorption from solution are observed for the stearyl series ranging from -16.7 to -7.14 kcal/mol analyte. The type and strength of the analyte-analyte interactions within the monolayer influence the ordering of the enthalpies of adsorption from solution. The patterns that the molecules in this series make in monolayers at the solution/HOPG interface have been rigorously studied using STM and two motifs are known. As stated above, octadecane, 1-bromooctadecane, and stearic acid assemble in a linear motif, and 1-octadecanethiol and

1-octadecanol assemble in a herringbone pattern. The two molecules which assemble in a herringbone pattern have the highest experimental enthalpies of adsorption from solution. The herringbone motifs contain an infinite one-dimensional chain of head-to-head interactions (Figure 3-5a and b). The MM optimized model of the 1-octadecanol monolayer displays an O···H-O angle (Figure 3-5a) of 172°, in line with expected behavior for hydrogen bonding.[48,49] This optimal geometry implies strong hydrogen bonding interactions along the infinite one-dimensional chain, and indeed 1-octadecanol gives the strongest enthalpy of adsorption and highest computationally derived lattice energy. The S···H-S angle (Figure 3-5b) of 128° for 1-octadecanethiol, consistent with the weaker nature of thiol hydrogen bonding, should yield a somewhat smaller enthalpy of adsorption and lattice energy, which is observed. The distorted angle in 2D is consistent with three-dimensional crystal structures for other terminal alkanethiols.[50,51] Nonetheless the infinite chain of donor-acceptor interactions in the two herringbone motifs correlate with the highest exothermic enthalpy of adsorption from solution for this series. The two least exothermic adsorption events are for the analytes which assemble in a linear pattern. Both octadecane and 1-bromooctadecane lack the functionality for hydrogen bonding and with the exception of one bromine atom are chemically similar to the solvent, n-heptane. The adsorption of 1-bromooctadecane is weak relative to octadecane. This can be ascribed in part to the fact that 1-bromooctadecane has a relatively high enthalpy of solvation in heptane (Table 3-4) and therefore pays a greater price for desolvation to adsorb from solution. It is the stearic acid adsorption, in a *pseudo*-linear monolayer pattern, which has an enthalpy between that of the analytes in the linear and herringbone patterns. While the incomplete interdigitation due to the steric hindrance of the terminal carboxylic acid group (Figure 3-5c) may contribute to a smaller enthalpy of adsorption for stearic acid, ranking the fatty acid in the middle of the series is, at first glance, surprising because hydrogen bonding in carboxylic acid dimers is stronger than in terminal alcohols.[49] However, adsorption from solution relies on more than absolute strength of analyte-analyte interactions, motivating the discussion of the role of solution-phase interactions below.

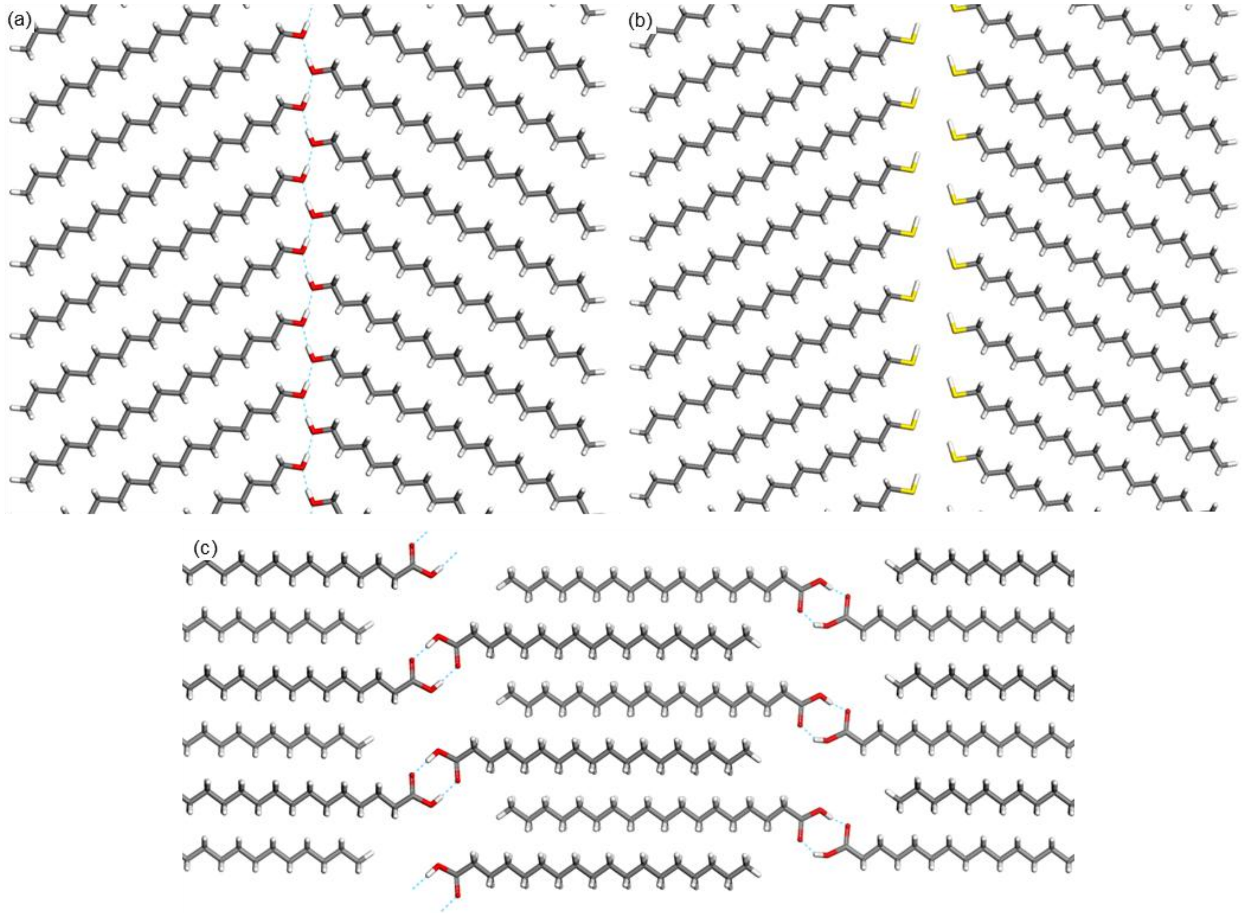

Figure 3-5 Molecular models showing the intermolecular interactions for (a) 1-octadecanol, (b) 1-octadecanethiol, and (c) stearic acid. The blue, dashed lines indicate hydrogen bonding. The alcohol and thiol terminated molecules for assemblies with infinite one-dimensional interactions. In contrast, the hydrogen bonding interacting in the assembly of stearic acid is cyclic dimers.

The analyte-analyte interactions present in each monolayer were investigated quantitatively using MM. Strikingly, without accounting for the role of solvent or substrate interactions the lattice energies do generally match the experimental enthalpies of adsorption from solution in both size and magnitude. This is most likely due to a balancing of the loss of solvent-substrate interactions (an endothermic event) and the formation of analyte-substrate interactions (an exothermic event) during analyte adsorption at the liquid/solid interface; both of these processes are ignored by MM. However, the order of the computed lattice energies for the stearyl series does not match the order of the experimental enthalpies of adsorption. Possible causes of this discord are now explored. First, one notable difference between the computational and experimental methods is that the lattice energy calculations do not take into consideration any role of the solution-phase interactions. Analyte-analyte interactions could occur in solution prior to adsorption and not only upon physisorption. Pre-assembly in solution would mean that lattice energies, which compute complete dissociation to isolated molecules, will overestimate the observed enthalpy of adsorption. Fatty acids are known to form dimers in nonpolar solvents,[25,52–56] and under the concentrations employed in this study a majority of the stearic acid molecules are expected to be dimerized.[56] Stearic acid is computed to have the second strongest lattice energy (Table 3-3) after the alcohol, whereas it falls near the middle of the experimental enthalpies of solution (Table 3-2); this suggests that the solution-phase formation of dimers (not accounted for by the lattice energy calculations) are thermodynamically relevant. It is possible that a greater accord between the enthalpies of adsorption and the computational results could be reached at much more dilute conditions because of the increase in the presence of monomers in solution. Not accounting for the role of solution-phase interactions limits the utility of lattice energies to estimate the enthalpy of adsorption at the liquid/solid interface. Similar trends in monolayer stability (alcohol > acid and alcohol > alkane) have been derived from temperature-dependent incoherent elastic neutron scattering experiments and have also assumed dimer formation of the fatty acid.[57–59] A second role of the solvent is to compete with the analyte for adsorption onto the substrate. This competition should lead to a less exothermic heat of adsorption from solution than anticipated based on gas phase adsorption studies.[60] The bromoalkane analyte has the potential for strong van der Waals interactions and would therefore be expected to have a higher enthalpy of adsorption than the alkane. This is the ordering predicted computationally (Table 3-3) and is in accord with gas phase desorption studies.[47] However, according to the experimental enthalpies of adsorption from solution, 1-bromooctadecane has the least exothermic adsorption energy. Both the higher penalty for desolvation of 1-bromooctadecane (Table 3-4) and the larger area per molecule in a monolayer relative to octadecane (Table 3-2) contribute to this difference in ordering between the computational and experimental methods. A complete understanding of the thermodynamics of adsorption at the liquid/solid interface is predicated on a nuanced understanding of the role of solvent and solution-phase interactions.

Table 3-4 Enthalpies of solvation from electronic structure calculations.

Analyte	Enthalpy of Solvation in Heptane (kcal/mol)
1-octadecanol	-12.2
1-octadecanethiol	-12.5
stearic acid	-12.8
octadecane	-11.0
1-bromooctadecane	-13.0

Conclusion

Flow microcalorimetry has been shown to be a powerful method to experimentally probe self-assembly at liquid/solid interfaces. Incorporating all intermolecular interactions relevant to the solution/solid interface in one experimental method reveals the limitations in using computationally derived lattice energy calculations to approximate the enthalpies of adsorption when solution-phase interactions are not accounted for. Both the calorimetry data and the computationally derived lattice energies rank the strength of interactions similarly: alcohol > thiol > alkane; the placement of the fatty acid and bromoalkane analytes in the ranking varies between methods. In order to correctly quantify adsorption strength at the liquid/solid interface, solution-phase interactions must be considered. With regard to the thermodynamics governing ordered, two-dimensional self-assembly, these findings have implications for selective adsorption in more complex systems where competitive interactions at the adsorbent-solution interface dictate the quality of separation achievable.

Future Directions

The stearyl series examined above showed the importance of accounting for solution-phase interactions when trying to understand the thermodynamics of self-assembly at the liquid/solid interface. Temperature-dependant FMC studies would allow us to obtain entropies of adsorption and thus free energies of adsorption, additional important features for a complete thermodynamic picture of adsorption. The FMC system is also well-equipped to study adsorption from the gas phase. For example, experimental heats of sorption of water for air-sensitive microporous coordination polymers could provide direct evidence for irreparable structural damage under humid conditions.

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Chapter 4

A Designed Professional Development Program to Encourage Graduate Student Instructors to Use Active Learning in Chemistry Discussion Sections

Introduction

National calls for improvement in science, technology, engineering, and mathematics (STEM) undergraduate education continue.[1–7] Policy, curricular reform, pedagogical reform, and faculty development utilize different routes, often pursued in parallel, to address this national need.[8] While a doctoral degree is a research degree, it is also the primary requirement to teach at the university level. Graduate student instructors (GSIs), who often function as the "teaching army" at large Universities,[9] often have more contact hours with undergraduates than faculty do,[10] and thus can have a large influence on undergraduate students' persistence in science disciplines.[11] Given this, professional development for GSIs geared toward helping them to become more reflective and practiced teachers is a prime opportunity to both improve undergraduate science education and prepare future faculty.

Current GSI training models are not well suited to the teaching and developmental needs of GSIs. No training is usually offered at the department-level due to a variety of constraints.[12] While experience alone can help GSIs grow as instructors, it is not enough to improve student learning.[13] I am working to capitalize on existing organizational structures related to GSI teaching positions for chemistry graduate students at the University of Michigan. To that end, I have designed what I am calling the active learning professional development program (ALPDP) to help support the GSIs in their teaching practices. The program goals are two-fold: first, to better equip the GSIs with pedagogical tools, and second, to begin and sustain a conversation in the department about teaching – the what, how, and why – to continue moving the department toward increased learner-centered instruction.

In addition to designing the program, I am researching the participating GSIs' learning in relation to their teaching. This research is an example of design-based research,[14–16] a genre of research that I explain later in this chapter. The research questions that guided my research are:

1. What do the GSIs "count" as active learning? How did they incorporate their images of active learning into their discussion sections?
2. What portions of the ALPDP do the GSIs think benefited their teaching practice the least/most? Why?
3. What assumptions about teaching and learning influence their perceptions of what was beneficial to them during the ALPDP?

Conceptual Framework

The fundamental ideas, theories, and assumptions held about the situation being studied are called the conceptual framework.[17] Such frameworks guide the shape, direction, and scope of related research questions. This research is guided by two frameworks, active learning and constructivism learning theory.

Active Learning

In the shift toward learner-centered education, active learning has been touted as a best practice in undergraduate education as early as the 1987 bulletin by the American Association for Higher Education.[18] In the simplest sense, active learning refers to classroom practices requiring student interaction and engagement in the learning process.[19] There are a wide variety of active learning strategies for classrooms, varying from simple to complex (Figure 4-1). Such strategies could include think/pair/share exercises, peer instruction,[20] exam-question writing, minute papers (check of student comprehension, interest, or opinions through anonymous, written response to an instructor-posed question), and discussions of old exam questions.[21,22]

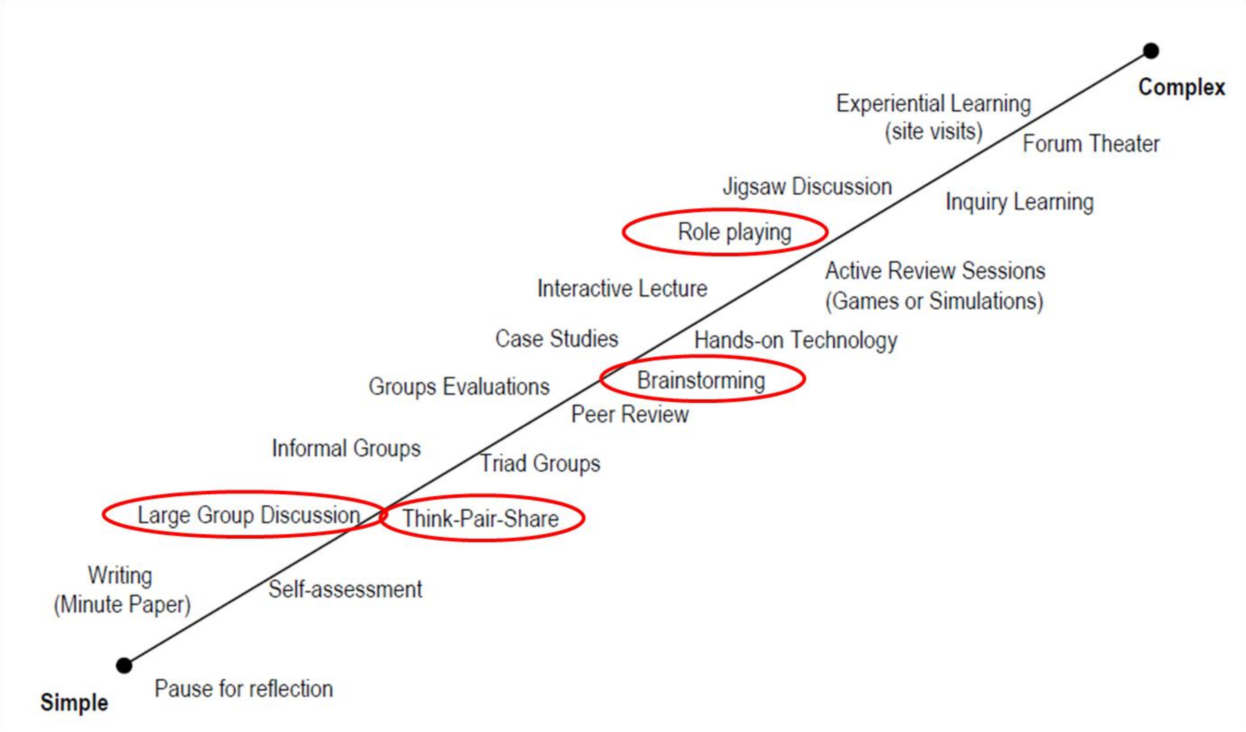

Figure 4-1 Adapted spectrum of some active learning strategies.[23] Circled activities were emphasized during the ALPDP.

While active learning strategies have become common in education reform circles as a way to increase student engagement, there is confusion in the field about exactly what is active in “active learning.” Anthony notes that active learning has been used to refer to both student-directed learning activities and deep mental engagement in the learning experience.[24] Additional challenges related to implementing active learning strategies include the sparse literature on active learning for the post-secondary level and resistance from both faculty[25,26] and students. Critical in making active learning strategies useful in service of encouraging increased student engagement and learning, is the need to help faculty learn how to implement such strategies in their classrooms.[27] To that end, I am studying the learning of a cohort of GSIs with respect to their teaching as they engage with the ALPDP that I designed.

Constructivism

In active learning strategies, like those described above, CHEM 130 students learn through engaging the material. This is a constructivist perspective on learning. Constructivist theories of learning, more specifically personal not social[28] constructivist learning theories, posit that learners assemble their own understanding of the materials. Central to constructivism as a philosophy is that the learner is not given knowledge or information (a transmission model of learning), but rather the learner gains knowledge through experiences that have meaning to the learner and through interaction with others.[28,29]

Constructivism is a theory of learning, but has implications for teaching. Baviskar et al.[30] outline "four essential features of constructivism" as a pedagogical approach for knowledge construction. Knowledge is a connected through a construct of information, experiences, and emotions and their relationship to each other. Prior knowledge must be elicited (first feature) for new information to be incorporated into the knowledge construct.[31] When new information does not fit within the existing construct, cognitive dissonance has been created in the learner (second feature). As Linenberger describes, "cognitive dissonance is the psychological state where the learner's attitudes, beliefs, or behaviors are at odds with one another."[32] The clash between new information and prior knowledge construct can be resolved by modifying the construct or discarding the new information. Creating cognitive dissonance is not sufficient alone to establish new knowledge. The new knowledge must be applied (third feature) to new situations to test the new knowledge construct. Such testing of the new knowledge construct allows the construct to be fine tuned and for repetition to reinforce the learning.[33] Reflection on what was learned, how it was learned, and why it was learned (fourth feature) ensures the endurance of the new knowledge in the construct. These features do build on each other but are not necessarily a singular, linear process.

From a constructivist stance, the role of the teacher becomes “Ask, don’t tell.”[34] Each of these four features of constructivism as a pedagogical approach are important features and are integrated in the ALPDP as outlined below.

Design as Research and Overview of Professional Development Program

Design-based research is a research methodology used to study learning theory, learning, and the natural environments in which learning occurs.[15,16,35] As such design-based research is a particularly useful method to study environments and artifacts including but not limited to curriculum innovation, museum exhibits, and teacher training. In design-based research, designs are conceived and implemented in their natural environment to test and inform theories about learning, teaching, educational reform, design, and designed artifacts.[16] The process of design-based research is marked by iterative cycles of design, implementation, analysis of data collected during implementation, and then revisions of designs based on data analysis.[15] One strength of this method of research is that it allows for authentic consideration of the learner, the information source (teacher, curriculum, museum exhibit, etc.), and natural environment. Bell adds that the authentic complexity inherent in design-based research is an important feature in sustaining and promoting innovation.[14] The complex nature of GSI responsibilities, undergraduate education, and teacher education make researching an educational ecology encompassing all three an ideal fit for design-based research. The various components of the ALPDP that I designed are outlined in Table 4-1. In the rest of this section, I expand on the components of the program.

Table 4-1. Summary of active learning professional development program activities.

Context	Activities
pre-semester professional development	demonstration discussion section
	discuss readings: active learning & teaching chemistry/science
	create list of "best practices in teaching"
	authentic GSI activities: plan a discussion section, write a quiz
	review quiz policies
	question and answer session: common issues with the undergraduates
	practice giving a discussion section
weekly meetings	*Regular activities*
	small group quiz checking
	brainstorm resolution to misconceptions
	develop connections with engineering and pre-health fields
	Representative supplementary activities
	reflect & discuss "what have you learned lately"
	"high" and "low" preceding week of teaching
	identifying easy and hard "best teaching practices"

Context for Professional Development Program

All new GSIs in the chemistry department at the University of Michigan take part in a mandatory, two-day training held in late August before classes are in session. The incoming GSIs in the chemistry department are divided by departmental administrators into groups so that they can be prepared to teach either organic or general chemistry courses (based on which course they are likely to teach). The final course assignments are usually made after the training has been completed. I have used the word "training" thus far because the focus of these days has historically been to introduce the GSIs to their course-specific responsibilities (e.g. writing quizzes, grading, checking lab notebooks, proctoring exams, holding weekly office hours, posting resources on course websites), and logistics related to these responsibilities (e.g. pace of course content, where to submit grades, number of quizzes, homework or quizzes per semester). This focus on the practical, course-specific information in GSI training is common practice in GSI training in science fields nation-wide.[36,37] During these two days of training there are also presentations by senior faculty members on such topics as professionalism and departmental expectations of instructors.

During August of 2013, I worked with the 29 new GSIs who would later be assigned primarily to teach lab (CHEM 125/6) or lecture (CHEM 130) general chemistry sections. This design focuses on the time spent specifically in preparation to teach general chemistry lecture discussion sections (CHEM 130) both during the two days of the pre-semester GSI training and in weekly meetings throughout the semester. As per department history, the portion of the training for the lab course was handled completely separately. In order to try and provide the GSIs with training beyond logistics – training that focused more on helping students in their sections actually learn – I designed a professional development program to insert into the existing GSI training. Additionally, I sought to continue to support the professional development opportunities for GSIs by creating a weekly meeting throughout their semester-long teaching commitment.

As I noted above, one defining feature of design-based research is cycles of implementation, data collection, reflection and analysis, and revision of the design.[15] In this first implementation, summarized in Table 4-1, I designed all activities to introduce the GSIs to active learning by way of a constructivist approach so that they could implement active learning strategies in their discussion sections. It is through the features of a constructivist pedagogical approach to learning described above, that I will present the design.

The Design: Pre-semester

I implemented the first iteration of what I am calling the "active learning professional development program" (ALPDP) in August of 2013 during the annual, two-day, mandatory training for GSIs teaching undergraduate chemistry courses for the first time. I ran the ALPDP in conjunction with two other co-facilitators who, while involved in the execution, were not involved in designing the program. This first iteration focused on active participation of the GSIs in authentic activities related to a CHEM 130 GSI's responsibilities, such as writing a quiz or planning a discussion section, and also included ongoing interaction through the fall 2013 semester. In this way, the ALPDP was designed to model the kinds of active learning that the GSIs could use with their undergraduate students in their discussion sections. These features (e.g., authentic activities, and first-hand participation in them, as well as on-going interaction as a way to continue to support learning) are identified as keys to enduring professional development.[38]

The first task was to begin accessing the GSIs prior knowledge as related to teaching and learning and create cognitive dissonance about these issues. I began the pre-semester training portion of the active learning professional development design by asking participating GSIs to imagine themselves as students in a discussion section, and then I facilitated a demonstration discussion section to model the educational environment of a discussion section. At the end of the demonstration discussion section, I directed them to a prompt in their handbooks where they could record any reflections, experiences, and questions based on the new experience. The following day we discussed their reflections on the discussion section and how, and possible reasons why, it differed from their own experience of general chemistry. A constructivist framework for active learning required me to attend to the GSIs prior knowledge as a first step in their learning about active learning methods and how they might implement them in their discussion sections.

A second way I sought to elicit and disrupt the GSIs' prior knowledge was through reading and discussing literature. After the demonstration discussion section, the GSIs were assigned to read two articles and a handout about active learning strategies for homework. One article elaborated on unique features of teaching chemistry at the university level,[39] and the second was a very cogent, accessible argument for thinking scientifically about science education.[40] When we gathered the following day, I posed questions related to the readings for small group discussion on a PowerPoint slide. An example of one such discussion prompt is:

> From Wieman, "I believe a successful science education transforms how students think, so that they can understand and use science like scientists do."[40] Do you agree or disagree? Why? Can you point to an example of transformation in your own scientific education? Describe the context and experience to your group.

This kind of work to broaden understanding through connecting to prior experience, information, knowledge, or assumptions is a hallmark of constructivism[41] and a foundational step to teaching about active learning.

The next step in a constructivist approach to pedagogy is to apply new knowledge with feedback. This application was done in two major steps with the GSIs. First I challenged them to think specifically about their teaching and brainstorm lists of best practices they wanted to incorporate into their teaching in the coming semester. After making the lists on the chalk boards around the room, I asked each group to share some practices from their list with the rest of the cohort to begin articulating and analyzing the (mostly implicit) assumptions and goals in teaching, as well as provide a benchmark for what practices they wanted to uphold before the competing priorities of research and coursework were introduced. Second, I tasked each group of GSIs to plan and execute a discussion section. Each group could select the chapter they wanted to focus on and was given textbooks, lecture notes, and a list of common student misconceptions as resources for their planning. Identifying student misconceptions involves eliciting the students' prior knowledge and creating cognitive dissonance, the two important features of constructivist pedagogy. Therefore, by having a list of common student misconceptions the GSIs could begin planning active learning activities to raise these important issues during their discussion sections. These GSIs received mentoring and coaching by experienced graduate student instructors, myself and two co-facilitators.

After a working lunch to finish planning their activities for discussion, I directed the GSIs in a more in-depth conversation about quiz writing in the context of CHEM 130. The GSIs are expert students, very familiar with taking quizzes in their prior experience in school, but as novice teachers[42] there is need for additional consideration of quiz writing as they begin to use their new knowledge about teaching and learning to write quizzes. To deepen their understanding of what does and does not constitute a "good" quiz, I included two example quizzes in the handbook each of which violated the course-specific quiz writing guidelines in terms of the number or type of questions. The co-facilitators then led a general conversation about some of the mechanics of quiz writing (e.g., non-breaking hyphens), some stylistic aids to help students (e.g., keep units on the same line as their associated values, use a table and not a list to compare values), and how quizzes are standardized in the course (e.g., maximum of two questions, ten points total, only whole numbers may be used in grading).

As the GSIs continued to work through applying their evolving knowledge about incorporating active learning methods into their teaching, I intentionally built in time for the GSIs to ask questions of the experienced instructors. While the GSIs had asked a lot of questions during their time working in small groups, from our prior experience teaching CHEM 130 we (the facilitators) knew there were other common issues with students that we wanted to raise and address with the GSIs before the semester began. To help raise some of these issues, we passed out fifteen questions that we (the facilitators) had brainstormed in advance for them to ask us as experienced instructors. Such questions included: “What should I do if I don’t know how to answer a student’s question during discussion?” or “What are some things you’ve changed over the semesters about how you teach? Why did you make those changes?” The written questions were interspersed with new questions from the GSIs allowing for broad reflections and feedback throughout the cohort of GSIs.

The final two activities of the pre-semester portion of the ALPDP focused on application, feedback, and reflection on learning. After each practice discussion concluded, I (or the facilitator in the room) had the GSIs leading the practice discussion and GSIs acting as students reflecting in turn on what went well and what they would do differently. After all of the practice discussion presentations had been given, I gathered the GSIs again to give them an opportunity to reflect on what they had experienced as well as answer any questions or concerns raised in the practice discussion sections. To capture some of their reflections on what they had learned I passed out a survey at the end of the pre-semester portion of the ALPDP. In the exit survey I asked them to rank items like their interest and confidence in teaching, the appropriateness of the length and scope of the professional development using a 1-5 scale (1 being not at all, 5 being very much). I also included on the survey space for short answer responses about what they thought would be the most and least beneficial part of the ALPDP as well as anything else they wish we had covered. The survey also served to promote the GSIs to reflect on their learning.

The Design: Weekly Meetings

Throughout the fall of 2013, I facilitated weekly staff meetings with the cohort of GSIs. During these weekly meetings our primary activities were to review each other's quizzes, brainstorm ways to troubleshoot common student misconceptions, and develop connections with the content and engineering and pre-health fields. While the need for quality control of the quizzes did take precedence in the weekly meetings, the "four essential features of constructivism" as a pedagogical approach remained part of our work throughout the semester. Specifically, application of new knowledge and reflection on learning were perhaps most prominent during the weekly meetings. For example, I incorporated an "ice breaker" one week in which I asked each GSI to share with the group something that he/she had learned in the past week. During another week's meeting, I asked the GSIs to share a "high" and "low" teaching moment from the past week. Supplemental to our primary activities focusing on the course content for the following week, I also created intermittent activities to enhance our conversations about teaching and learning. For example, mid-semester I brought a handout with the lists of best practices the GSIs had generated during the pre-semester professional development activities and asked each GSI to identify and then discuss two of the practices that they found easy to implement and two that they found challenging, and why.

I designed each piece of the ALPDP around constructivist pedagogy. In accord with the professional development literature,[38,43,44] I relied on activities which are authentic to the GSIs' roles and responsibilities. Next, to describe how this research was conducted, I introduce the methods and analysis used.

Methods

As I discussed in the introduction, the ALPDP is design-based research; I am studying both the design of the program, and the GSIs learning with respect to their teaching as related to the design. Design-based research can be solely qualitative or involve mixed methods depending on the research questions.[15] As Zeichner points out, to research teacher training, personal experience with the training and qualitative research methods are both necessary; surveys are inadequate by themselves to access the complexities inherent in teacher training.[45] The forced choices in quantitative research allow "what" questions to be answered, and are especially useful when faced with extremely large data sets allowing for general trends to be found.[17] Through qualitative research we can answer "how" and "why" questions to gain a more nuanced understanding of the topic or question of interest.[17,46] Thus to deeply investigate issues like the GSIs conception and use of active learning strategies, I chose to use qualitative methods in this study.

Surveys

The first iteration of the pre-semester included twenty-nine new GSIs ten of which went on to teach CHEM 130 in the fall semester of 2013. These ten GSIs were joined by six GSIs who had taught CHEM 130 at least one previous semester. The department does not require GSIs to participate in GSI training annually, and so these "experienced" GSIs did not take part in the 2013 pre-semester professional development design. I collected entrance and exit survey data from the twenty-nine participants in the pre-semester design. I used the entrance surveys to probe the GSIs interest and confidence in teaching, conception of active learning, and personal expectations for the training. In the exit surveys, I also asked them what they thought would be the most and least valuable information and practice to them as GSIs and if they wanted any additional resources. I collected data at the end of the semester using a survey very similar to the exit survey I used at the end of the pre-semester portion of the ALPDP.

Interviews

I invited each of the sixteen GSIs from the Fall 2013 cohort to participate in interviews about their experiences participating in the ALPDP. Of the sixteen GSIs, nine chose to participate in interviews. Of the nine GSIs I interviewed, two had taught CHEM 130 before (and therefore did not participate in the pre-semester portion of the ALPDP) and four are female. Each interviewee was personally involved in teaching CHEM 130 and actively participated in some portion of the active learning professional development. While the interviewees provided rich descriptions of their experience teaching CHEM 130, the findings must be interpreted in light of a small sample size. Attempts to generalize outside of the given setting should be done with sensitivity to differences in setting and context. To maintain confidentiality with the interviewees, all names used in the chapter are pseudonyms.

My interview questions covered topics such as the GSIs' analogies for teaching and learning, conceptualization of active learning, and value of the pre-semester and weekly professional development. I developed interview questions based upon my research questions, and prior experience teaching CHEM 130 as a GSI, reading the literature, and implementing the professional development design. The semistructured interview guide that I developed and used in my interviews is available as an appendix to this thesis. The interviews were semistructured in nature,[46] meaning that I began with a set list of interview questions related to my research questions but was free to ask clarification questions of the interviewees and pursued interesting, emergent topics with the interviewees if and when they arose. I audio recorded the interviews in person in February of 2014, after the conclusion of the semester-long teaching experience. The data consists of semistructured interview responses with participating GSIs focusing on the GSIs experiences. Each interview lasted forty-five minutes to two hours and was audio recorded with the permission of the interviewee. Each digitally recorded interview was transcribed to provide an accurate record for analysis.

Data Analysis: Coding

As part of qualitative data analysis, the ongoing analysis is continually reviewed to check for validity.[46] To address issues of validity within my study, I cross-checked the themes across the interview transcripts. I also sent the preliminary findings back to the participants to see if it "rang true" with them (a process called member checking). When possible, I used data triangulation, using multiple data sources to probe the same theme or finding, to provide thick support for the findings.

Each interview transcript was coded for reoccurring themes related to my research questions.[46] For example, the GSIs described what they and their students were typically doing during discussion, the GSIs' thoughts about what they thought they should be doing and why, their own educational history, and their evolving expectations of students. I used themes that emerged from such discussions (e.g. role of GSI, goals for discussion, assumptions about students, and changes in teaching practice) as codes to group together related texts for a given theme. From a constructivist framework for learning, each of these themes begins to reveal through what prior knowledge, cognitive dissonance, and application of new knowledge (active learning) the GSIs exemplified in their practice (namely, discussion sections).

During coding, the themes emerged from the interview transcripts both within and across individual interviewees. I developed the themes based not upon the interview questions, but on the responses given. If several points were made within one sentence or "paragraph" of speech, I coded these points separately. Once I had finished the initial coding of each transcript (inductive analysis), I analyzed the text for a given theme/code from all of the interviews (deductive analysis). I based my findings on these themes across the interview transcripts. The findings explored below do not represent the sum total of what could be learned from the rich data set collected (interview transcripts, surveys, student evaluations of teaching). Rather, I chose to focus on findings related to my research questions, the aforementioned conceptual frameworks, and future iterations of the ALPDP.

Results and Discussion

Images of Active Learning

Central to the goal of my ALPDP is the GSIs' understanding and acquisition of pedagogy, as specifically related to the employment of active learning strategies. As stated above in research question one, I wanted to learn how the GSIs thought about active learning and incorporated their thoughts, images, and impressions of it into their discussion sections. At the end of the pre-semester portion of the ALPDP, the GSIs had begun to articulate a shift in their images of teaching beyond of that of traditional, lecture methods. As Joe, a new GSI, noted in his exit survey from the pre-semester portion of the design, "the emphasis on active learning made us re-evaluate the 'lecture' attitudes we apparently default to." The GSIs' ideas of teaching and learning however were not completely transformed. While most GSIs articulated some idea about what they thought active learning meant in the surveys and interviews, there was variation in how the GSIs thought about the importance of incorporating into their discussion sections pedagogical techniques to promote active learning. For example, Mark, a new GSI, spoke at length during his interview about what he thought active learning looked like in students and how he strove to support that kind of classroom environment. As Mark describes, a student engaged in active learning is

> …a student who has evaluated the problem at hand and is not waiting to be shown how to do it. A student who is talking to other students about ways they might approach the problem. A student who is possibly maybe even looking through some sort of references like a textbook for instruction or hints on how to approach a certain problem…. I think I try to encourage active learning by making them work in groups…. Certainly there can be active learning if they're working by themselves and just talking to me but I think by putting them in groups distracts them from me. It gives them something else to direct their attention to especially if they have questions or they're trying to bounce ideas off of somebody. So I think that the group work is an integral part.

To Mark, active learning involves the student deeply engaging the course material and he structured his discussion sections around group (peer) interaction to help facilitate such engagement. Alternately, Ben, another new GSI, connected the idea of active learning with worksheets and was intentional to not use multiple choice questions on his worksheets "so you can't just go through the motions."

What might account for this variation? First, the GSIs' conception of active learning reflected the less-than-precise use of the term in the literature, which encompasses both activities that require participation and those that initiate [deeper] mental engagement.[24] Many of the GSIs had heard about active learning from friends, their own reading, or their experiences as a student prior to encountering it in the ALPDP. In the surveys at the end of the semester-long portion of the program, GSIs were asked "What does 'active learning' mean to you?" The GSIs described a student's role in active learning as participating in their learning through mental engagement or any vocal class participation. They also described their role in active learning as instructors. For example, they saw their role as leading the students to correct conceptual understanding, not solely conveying content, and making the students answer their own questions. While lecture sections can be designed to support effective student processing,[47] the GSIs were drawing a contrast to lecturing as teacher-centered exposition. There was no homogeneity in how they described active learning and this mirrors the variation seen in the level of importance that the GSIs put on incorporating active learning strategies into their discussion sections.

In the interviews with the GSIs, there was again variation in how the GSIs talked about active learning. Mark, a new GSI, described active learning in his interview in terms of a scenario in which "a student … is taking the resources that they have at hand, trying to use them to understand what's happening." To facilitate this strategy in his discussion sections he required students to work in groups on a worksheet so that they would have to talk to each other about what they were doing. In contrast, Abbey, also a new GSI, talked about active learning in terms of how the students and GSIs interact in the classroom. In contrast to a lecture, Abbey described active learning as "more like interaction[,] so the teacher would just lead students to learn and not, push students to learn." The two GSIs who had taught CHEM 130 prior to the fall 2013 semester, and thus had not participated in the pre-semester portion of the ALPDP, had the least prior exposure with active learning and had a very loose conception, if any idea, what I meant when I asked them about active learning in the interviews. Again, while most of the GSIs had some way to talk about active learning in the interviews, in general the GSIs did not talk about active learning as a central or pivotal part of how or why they teach. Instead, as will be explored in later sections, their images of teaching came primarily from their (long) history as students.

This variation in how the GSIs talk about and implement active learning in their discussion sections raises a new research question for future studies: why is there this variation? In their development as instructors, most of the GSIs are transitioning from being expert students into the role of novice teacher.[42] A variety of factors such as motivation, prior teaching experience, educational background, and professional goals could support or stifle this development. After understanding such motivational and experiential factors we can then incorporate support for these specific aspects of GSI development and continue to move towards a robust program for teaching active learning strategies and encourage implementation of these strategies in CHEM 130 discussion sections.

From the literature, we know that professional development needs to be long-term and ongoing.[38,44] Change in teaching practice can continue over several years,[48] and thus we might expect less variation in future iterations of the ALPDP if the same GSIs are involved through multiple cycles. From a constructivist perspective of learning, learning also takes time; creating cognitive dissonance about prior knowledge is an early, critical step in learning from a constructivist perspective.[30] From the breadth in understanding of active learning after this program with the GSIs, we also see that creating dissonance about their image of “teaching as telling” also takes time and requires ongoing learning. I did not expect the process of dissonance, application, feedback, and reflection to be completed through one cycle of either the pre-semester or weekly professional development portions of the program. I discuss what implications this breadth in understanding among the GSIs has for future iterations of the design with other implications for future iterations at the end of this chapter.

Benefits of ALPDP to Teaching Practice

As design-based research, my research goals for this project are to not only inform learning theory (e.g. active learning and constructivist pedagogy) but also the next iteration of the design. To address this and my second research question, the GSIs were asked about what they found helpful to them and additionally how they would help prepare a new GSI to teach CHEM 130.

Activities in the pre-semester portion of the ALPDP incorporated all four steps of the constructivist pedagogy to help the GSIs learn active learning strategies: elicit the learner's prior knowledge, create cognitive dissonance with the learner's prior knowledge, insist that the learner apply their new knowledge, and finally reflect on their new learning.[30] Both in the exit surveys at the end of the pre-semester and weekly meeting portions of the ALPDP and in the interviews with the GSIs, the GSIs indicated that the activities most closely aligned with authentic, unfamiliar GSI responsibilities (e.g. writing quizzes and lesson plans) were helpful to them in their teaching practice. For example, Shawn, a new GSI, thought that "making the quizzes as a group was actually [closer to the reality of what we do] because, I mean we helped review quizzes [in the weekly meetings]. We see each other's quizzes and we take ideas from them so it is not too far removed." Other practices such as the demonstration discussion section and practice in planning for and executing a discussion section were also noted as beneficial parts of the pre-semester ALPDP by the GSIs. For example, as Ben said in his interview,

> I think the mock discussion was helpful. 'Cause I don't know about most students here, I know a lot of them came from small schools, I came from a smaller school. We didn't have discussions. So I had no idea what went on. I mean obviously

> [general chemistry lab], we all had that hopefully or some sort of version of it. But I don't know if everyone has discussions.

The feedback about the pre-semester portion of the ALPDP was mostly positive. The GSIs suggestions for improving the pre-semester ALPDP centered around constraints set on the training by the department and seeking additional, early practice in authentic GSI responsibilities. The GSIs are introduced to both the lab (CHEM 125/6) and lecture (CHEM 130) courses over the two days of pre-semester training and do not know during the training which they will be assigned to teach. Shawn expressed in his interview that he “would have found it more useful to know earlier on whether I was in lab or teaching. I could have focused more on the teaching or the lab aspect if I knew.” In the exit surveys from the pre-semester ALPDP, a couple of the GSIs also expressed that it was really hard to plan a discussion section in the time given (<2 hours). Mark also suggested adding a “quiz writing seminar” to the ALPDP with more specific training in making an easy question harder or longer.

Every GSI mentioned that quiz checking in the weekly meetings were helpful, but for a variety of reasons. Ben indicated that the “quality control on the quizzes [was helpful] 'cause that is the only thing kids are gonna’ complain about.” Shawn was also a supporter of the weekly quiz checks because he wanted feedback on the difficulty of his quizzes and to learn from other people’s quizzes what kinds of questions they were using in their sections. Reviewing common student misconceptions for the following week’s chapter was also noted as beneficial to the GSIs practice. For example, Al pointed out in his interview that the misconception sheets were helpful because “it is good to kind of just go over that in a group. And say, ‘Oh yeah, that’s right. I forgot about that.’” The major revision that the GSIs suggested for the weekly meetings is to eliminate the conversation about making connections between the following week’s content and engineering and pre-health fields. The GSIs said that they rarely used the connections we brainstormed primarily because their students never inquired about the usefulness of the course content for future coursework or careers.

What might cause these authentic practices to be of particular value to the GSIs? One idea is that in the GSIs development as novice instructors' activities in line with skills and knowledge appropriate for a novice teacher were perceived to have the most benefit to teaching practice. This construct of master student and novice teacher have implications for what the GSIs assume about teaching and learning, a subject I explore further in the next section.

Dual Roles of Student and Teacher

The ecology of a CHEM 130 GSIs teaching practice is complex. The GSIs are balancing the expectations of their students, the course-specific responsibilities as instructors, expectations of themselves as instructors, as well as their graduate-level course work and independent research. In as far as they tried to fulfill their pre-existing idea of what it means to be an instructor, they also projected their own history as a student onto their students. The GSIs' students may not have similar behavior, goals, or outcome as the GSIs did as students. Relevant to the third research question, participating GSIs discussed their dual roles of teachers and students and the influence of them on their teaching practice. They discussed experiencing teaching as a student that they did not count as helpful to their own learning, but then were aware that they utilized those very same techniques when they were in the role of "teacher." For example, consider the following quotation from an interview with Mark:

> We've also been through this system that's told us exactly what a teacher is from the students' perspective….There is a category in your brain of expectations you have for a teacher, and what a teacher does and what a teacher doesn't do. And

> now that you have been thrown into that role of teacher, you unconsciously and un-objectively adhere to those standards that you have set for what exactly a teacher does, what a teacher should do, what a teacher shouldn't do and how a teacher does it…. Sometimes you do things as a teacher because they are "teacher" thing[s] to do. And the next day you're a student and you're sitting in [your class] and you're like, "Oh my, God, that's the worst thing ever. I'm not even learning anything right now." And then you go and might do it as a teacher the very next day -- or you just did it yesterday as a teacher…. I think it serves as an extremely valuable experience to be both an explicit teacher and explicit student at the same time because that allows us to try to … [a]ssess teaching from a student's perspective and a teacher's perspective at the same time so that you can actually change your own perspective on it as a teacher to match what is good for a student.

From a constructivist pedagogical stance, these dual roles of student and teacher, while potentially frustrating in graduate coursework, can benefit the GSIs by strengthening their cognitive dissonance about teaching and learning and thus support their development as instructors and implementation of active learning in their own classrooms.

GSIs' decisions about how to clarify the content reflected the challenges they experienced with similar content when they were students. John brought this up in his interview as we discussed about knowledge and skills important for new GSIs to learn:

> Go back; what really pissed you off in the book when [your instructors] explained something to you because it didn't make any sense? Now, you intrinsically understand it a much better way, explain it that way and you'll get rid of about

> 90% of the problem I would say with just getting them onto the right track of looking at it.

I did direct the GSIs to spend time during the pre-semester ALPDP thinking about teaching in light of their prior experiences as a student. It was assumptions about teaching based on their experience as a student which influenced their use and perception of the usefulness of the ALPDP. No GSIs reported that they found the content challenging (they are expert students after all), but they did express that being introduced to the course logistics (e.g. pace of quizzes, acceptable reasons to give a make-up quiz, keeping current with the heavy grading load) and student management during the pre-semester professional development module was helpful preparation for teaching. As Abbey noted in her interview,

> The class is intro chem so it's stuff that I should have to review it a little bit, but it's not the chemistry that is the part that you aren't comfortable with - it's the being in front of a classroom looking at you. When you ask them a question and they just stare at you. So it was nice to know this might happen, here's what you do if it does.

As Abbey described, the question and answer time of the pre-semester portion of the ALPDP was helpful in the GSIs understanding of their responsibilities and preemptively addressing some of the common, practical issues they experienced in their teaching practice.

The GSIs assumptions and related decisions about teaching flow directly from their prior experience. As Sandi-Urena found, GSIs self-image is constructed from their prior experience as a student, their beliefs about the nature of knowledge, their beliefs about the nature of the instructional context (laboratory or lecture), the learning environment, and their training and support.[49] In a constructivist learning theory all of these factors are part of the mosaic of prior knowledge that the GSIs bring into their teaching practice. As Austin said, "GSI development is shaped by many factors that take place in a nonlinear, complex way,"[50] and a pedagogy for active learning strategies must be sensitive to the various influences in the development of teaching practice. This was also seen above in the heterogeneity of the GSIs conception and integration of active learning strategies in their discussion sections.

The professional development literature emphasizes the importance of longevity for lasting development to occur.[44,51] Wyckoff found that gains in instructor effectiveness (as defined by student performance on a standard exam) increased over four years of work toward more interactive classroom instruction.[48] I did not expect that two-days of professional development work would alone completely alter the GSIs images of "teaching as telling" from their own time as students. These images of teacher as a master student probably originate, not from the ALPDP, but from the GSIs long history as students. Working to externalize implicit or prior knowledge is the first step in a constructivist pedagogical stance and was an activity early on in the pre-semester ALPDP (Table 4-1). Abbey noted in her interview that she found making and discussing the lists of "best practices" helpful to get her thinking about positive teacher practices to exhibit in her teachings like writing everything out on the board and the pace of the class that she normally did not think about in her role as a student. Implications for this strong teaching connection with the GSIs' student history in the second iteration of the program are discussed below.

Concluding Remarks and Implications for Next Iteration of Design

I designed the active learning professional development program using constructivist pedagogy. Working within the time constraints of the departmental GSI training program, I crafted an experience for the GSIs to learn about active learning pedagogy through being engaged in active learning about CHEM 130. From this first iteration of the ALPDP, there was heterogeneity in how the GSIs talked about active learning and its importance in how they taught in their CHEM 130 discussion sections. In future iterations of the ALPDP, the emphasis on active learning strategies could be strengthened in both parts of the program. In the pre-semester portion of the ALPDP, I could explicitly require the GSIs to choose one of the active learning strategies and incorporate it in their practice discussion section. This would allow them to examine, test, and reflect on one or more of the strategies early on in their teaching practice. One of the weekly meetings could be exchanged for a seminar about active learning strategies facilitated by the teaching and learning center on campus. This interaction in the middle of the semester would help to provide additional opportunities to explicitly think about and practice active learning strategies with feedback.

The portions of the pre-semester and weekly ALPDP that the GSIs did feel benefited their teaching practice were closely aligned with understanding what is in a discussion section (e.g. the mock discussion section) and practicing skills relevant to that context (e.g. lesson planning, practice discussion section, and quiz writing and checking). It became clear quickly after the pre-semester portion of the ALPDP that an essential GSI responsibility had not been developed: grading. This could easily be incorporated in the next iteration of the design by having the GSIs all grade the same quiz and comparing how they scored the quiz. This kind of conversation, practice, and reflection around an essential (CHEM 130) GSI skill would be another layer of a constructivist cycle of learning about teaching embedded in authentic practices.

The GSIs assumptions about teaching, that mastery of content as critical for teaching success, reflect their prior experience as expert students and not constructivist pedagogy or active learning. One way to provide additional examples of discussion sections which incorporate active learning methods would be to create a mechanism for new GSIs to attend and reflect on more experienced GSIs discussion sections early in the semester. Alternately, the cohort of GSIs could work together to plan, refine, and execute a single discussion section exemplifying a particular active learning technique; this practice is commonly called lesson study.[52] The GSIs simultaneous role as student could also be leveraged to further establish the difference between a traditional classroom and one that uses active learning strategies.

Active learning methodology is popular among educational reform teams but lacks clarity in the literature. How do we teach pedagogical content knowledge, especially active learning? This work suggests that a strong constructivist framework and activities authentic to the teacher's work are good starting places in teaching active learning strategies to teachers. The professional development literature for science teachers emphasizes that ongoing interaction is necessary for development in teaching practice to occur.[38,44,51] This was challenging given the departmental time constraints for GSI training. Capturing the GSIs development throughout the semester through artifacts collected in these cycles will be helpful in developing further iterations of active learning professional development and a robust understanding of how to teach active learning methods.

As we continue to learn how to teach active learning strategies, the insights into the roles of instructor assumptions in incorporating such strategies and program needs and constraints discussed above will be important in directing future research in this kind of teacher training. In working with graduate students, this work highlights the need to account for the breadth of their prior knowledge and experience as well as their process of developing as instructors. To develop graduate students as instructors, as the professional development literature says,[38,44,51] long-term opportunities are important for lasting change. While the intent was primarily to provide GSIs with pedagogical tools, there is great potential to impact hundreds of undergraduate students through helping GSIs learn to incorporate deeper student engagement in their discussion sections and such impact will be interrogated in future research with iterations of this program.

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APPENDIX

Semi-Structured Interview Guide for Active Learning Professional Development Program

This document contains sample interview questions that I asked during the semi-structured interviews conducted with graduate student instructors. As is typical during semi-structured interviews, I did not word these questions exactly as I've written them below, or use them in this order. If during the course of the interview, interesting lines of discussion appear that are pertinent to the study, I asked additional questions to follow these threads.

1. Tell me about a typical CHEM 130 discussion section that you taught. What were you doing? What were your students doing?
2. Talk to me about what it's like to teach. What analogy or picture would you use for what it's like to teach?
3. What was critical in your success as a GSI last semester? What was most helpful?
4. What are your (current) career goals? Do you see teaching as part of your preparation for that career? If so, how? If not, why?
5. Had you heard the term "active learning" before the GSI training in August?
6. Now that you've taught CHEM 130, what sorts of things would you tell a new instructor to best prepare him/her for teaching undergrads here? What things would you do with a new instructor to prepare them for their job as a CHEM 130 GSI?
7. What supports in the weekly (staff/PD) meetings were helpful to your work as a GSI? Why was it helpful? What wasn't helpful, and why?

8. We regularly tried to brainstorm ways to connect course content to pre-health and engineering fields. Did you use any of these brainstormed ideas in your discussion sections? If so, how? If now, why?