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Protonation, Hydrolysis, and Condensation of Mono- and Trifunctional Silanes at the Air/Water Interface

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Abstract

The protonation, hydrolysis, and condensation kinetics of octadecyldimethylmethoxysilane (OMMS) and octadecyltrimethoxysilane (OTMS) at the air/water interface were investigated using a monolayer trough. OTMS chemical condensation within physically condensed phases was observed in transferred monolayers using fluorescence microscopy. Molecular area increases and decreases attributed to protonation and hydrolysis, respectively, of silane methoxy groups were measured by a surface balance. These area changes at constant surface pressure suggested a stepwise protonation and hydrolysis of the three OTMS methoxy groups. In contrast, only a single protonation and hydrolysis event was observed for monofunctional OMMS. The influences of monolayer spreading time, silane packing density, and subphase pH on the reaction kinetics are presented.

Introduction

The use of the monolayer trough as an instrument to monitor the hydrolysis kinetics of alkoxysilane amphiphiles has recently been demonstrated by several authors.^{1–3} The trifunctional silane OTMS ($\text{CH}_3(\text{CH}_2)_{17}\text{Si}(\text{OCH}_3)_3$) employed in these studies is well suited for interfacial kinetics experiments given its relatively slow chemical reactivity at the air/water interface. Furthermore, OTMS hydrolysis is easily monitored at the interface as its polar headgroup undergoes a 50% decrease in molecular area (from 40 to 20 Å²/molecule) when all three methoxy groups are replaced with hydroxy groups.² Since chemical condensation among hydrolyzed OTMS molecules does not greatly influence the molecular area, a separate technique such as fluorescence microscopy is necessary to follow condensation.^{1,2}

The monofunctional silane OMMS ($\text{CH}_3(\text{CH}_2)_{17}\text{Si}(\text{CH}_3)_2(\text{OCH}_3)$) has also been studied for its simplified interfacial hydrolysis and condensation (dimerization) kinetics compared to OTMS.³ For both silanes the interfacial reaction kinetics were monitored either through changes in molecular area or changes in surface pressure (π), with time. These studies have reported that the hydrolysis and condensation of OTMS on aqueous subphases generally followed a reaction mechanism which initially proceeded slowly, abruptly accelerated, and

then slowed again as it neared completion.^{1–3} This “slow–fast–slow” kinetic behavior was attributed in part to a difference in hydrolysis rates for the three methoxy groups per OTMS molecule.² For bulk solution sol–gel kinetics, it is reported that as methoxy groups are substituted by hydroxy groups on the silicon site, hydrolysis of remaining methoxy groups on the site becomes progressively faster.^{4,5} Although a similar trend of enhanced hydrolysis rates may be anticipated at the air/water interface, additional factors such as molecule conformational freedom, packing density, and accessibility to nucleophilic attack from the subphase must also be considered. The interfacial silane hydrolysis kinetics published thus far have provided only a general (slow–fast–slow) picture of the process.

A multitude of techniques have been employed to confirm that OTMS hydrolysis and chemical condensation is indeed occurring at the air/water interface. XPS analysis of OTMS monolayers transferred after various times at the air/water interface clearly showed the disappearance of the methoxy (C–O) signal as hydrolysis proceeded.³ Condensed domain morphology and size distribution were obtained with scanning force microscopy (SFM) analysis of octadecyltrichlorosilane (OTS) monolayers transferred in the coexistence region of the liquid-expanded (LE) and liquid-condensed (LC) phases.⁶ High-resolution SFM and FTIR analysis of OTMS monolayers indicated an almost vertical molecular-orientation with molecular areas near 16 Å²/molecule for monolayers transferred at surface pressures of 25 mN/m.⁷ OTMS condensed domain formation was also monitored in-situ using fluorescence microscopy, which suggested chemical condensation at the air/water interface begins immediately after hydrolysis.^{1,2} Monitoring hydrolysis rate and condensed domain size and geometry as a function of pH demonstrated that under basic conditions condensed domains formed smaller “flocklike” structures, while under acidic conditions larger “star”-shaped structures possessing 6-fold symmetry formed.¹ However, these domains were allowed to form under constant area conditions in which surface pressure was allowed to change; thus, the effects of monolayer packing density on hydrolysis and condensation were not controlled. In addition, the cited SFM studies of silane-condensed domain morphologies have all employed a vertical dipping method in which dewetting during monolayer transfer is known to influence domain size and shape.⁶ Thus, further investigation of OTMS hydrolysis and condensed domain formation at interfaces is warranted.

Our interests in creating surfaces in which the size, shape, and distribution of chemically condensed domains or defects in monolayer films can be controlled has lead us to investigate Langmuir films of functional organosilanes at the air/water interface. In this paper the experimental conditions which must be met to optimize sensitivity and control over the protonation, hydrolysis, and condensation of OTMS and OMMS monolayers at the air/water interface are discussed. The experiments presented here demonstrate that monolayer spreading and solvent evaporation times, amphiphile packing density, and subphase pH dramatically influence silane hydrolysis and condensation kinetics. Control of these experimental parameters has allowed for more detailed reaction kinetics, possibly corresponding to a stepwise protonation and hydrolysis of methoxy groups, that are attained using the surface balance.

Experimental Section

Materials

Octadecyltrimethoxysilane and octadecyldimethylmethoxysilane (>97% purity, United Chemical Technologies) were diluted to 1 mg/mL in chloroform (EM Science, spectroscopy grade) and stored at -20°C . Double distilled water (pH 5.6, $\gamma(20^{\circ}\text{C})$ 72.8 mN/m) and phosphate buffered saline (PBS) were used as the subphases. The 10 mM PBS, pH 4.3, subphases were prepared from monobasic and dibasic sodium phosphate salts, which were adjusted to 150 mM ionic strength with sodium chloride and potassium chloride. Fluorescence microscope analysis of transferred OTMS monolayers was achieved by staining with 0.003 mg/mL solutions of horse spleen ferritin (Sigma) labeled with tetramethylrhodamine isothiocyanate (TRITC, Molecular Probes). Contrast thus provided was based on monolayer packing density and charge character effects on ferritin adsorption. At pH 5.6 rhodamine-labeled ferritin (Rh-Fer) preferentially adsorbed on the less densely packed phases in the monolayers and/or the regions of neutral or positive charge (ferritin isoelectric point is at pH_{iep} 4.5). Monolayer staining was preferred to the introduction of an amphiphilic dye at the air/water interface due to the potential influence of the dye on the hydrolysis and condensation processes.⁸ Hydrophobic glass coverslips (VWR) were used as substrates for monolayer transfer. Coverslips were made hydrophobic using OTS silanization protocols.⁹

Langmuir Trough

Monolayers were prepared on aKSV5000 “tandem” trough (KSV Instruments) housed in a dust-free cabinet placed on an antivibration table (TMC). The trough and barriers were thoroughly cleaned with absolute ethanol and rinsed for 10 min with deionized water, followed by double distilled water. The surface pressure was measured using a platinum Wilhelmy plate attached to a surface balance (resolution $\sim 4 \mu\text{N/m}$) (KSV). The platinum Wilhelmy plate was rinsed with ethanol and passed through the flame of an alcohol lamp and then rinsed with double distilled water. The subphase was maintained at 20°C using a circulating water bath, and the pH was monitored using a pH electrode (Radiometer). A second surface balance was placed in the other trough (troughs connected through the subphase) to correct for subphase evaporation during extended experiments. Prior to monolayer spreading the interface was aspirated clean until the surface pressure changed by less than 0.1 mN/m upon reduction of the interfacial area from 850 to 50 cm^2 .

Monolayer Spreading

OTMS or OMMS solutions were rapidly spread ($70 \mu\text{L}$ in 1 min over 850 cm^2) on the subphase and were allowed to incubate for a fixed time (t_0 : 0–1 h) at zero surface pressure before being compressed to a given surface pressure. Rapid compression rates ($25 \text{ \AA}^2/(\text{molecule min})$) were used such that the reactions could be monitored quickly after spreading. At this compression rate it was possible to begin monitoring the reactions within 2.5 min after spreading the first drop of solution at the interface (1 min for spreading $70 \mu\text{L}$ + 1.5 min to reach the feedback pressure).

π -A Isotherms

OTMS monolayers were cycled between 0 and 30 mN/m at a rate of $\pm 4.4 \text{ \AA}^2/(\text{molecule min})$. OMMS monolayers were cycled between 0 and 25 mN/m at a rate of $\pm 8.8 \text{ \AA}^2/(\text{molecule min})$. Between successive compression/expansion cycles, the monolayer was maintained at zero surface pressure for either 1 (OMMS) or 20 (OTMS) min. Data are presented as successive compression isotherms.

$A(t)$ Isobars

Monolayers were compressed to the desired feedback surface pressure, and changes in barrier position and velocity with time were recorded. Results are presented as molecular area vs time.

$\pi(t)$ Isoarea Curves

Monolayers were compressed to the desired molecular area, and changes in surface pressure with time were recorded. Results are presented as surface pressure vs time.

Monolayer Transfer

Transferred monolayers with polar headgroups facing the ambient were obtained using the horizontal transfer method in which a hydrophobic coverslip oriented parallel to the plane of the interface was pushed into the subphase. To avoid disrupting the monolayer orientation, transferred films were maintained hydrated in a fluid cell during fluorescence microscopy analysis.

Transferred Film Surface Analysis

Fluorescence microscope images were obtained using an inverted microscope (Diaphot 200, Nikon) equipped with 40 $\times$ NA 0.65 and 100 $\times$ NA 1.25 oil-immersion objectives (Leitz). Images were recorded using the MicroView imaging system (Princeton Instruments).

Results

I. Trifunctional Silane Kinetics

OTMS π -A Isotherms—Successive π -A isotherms for OTMS on H_2O , pH 5.6, are presented in Figure 1. The monolayer incubation time (t_0) at zero surface pressure was 10 min. Numbers on isotherms indicate the order in which they were attained. The isotherms were recorded over a 24 h period, and the average elapsed time between isotherms was 46 min. The first several isotherms demonstrate a plateau centered near 11 mN/m which corresponds to a liquid-expanded to liquid-condensed (LE-LC) phase transition. A second plateau at 20 mN/m, corresponding to a liquid-condensed to solid-condensed (LC-SC) phase transition, is also evident in the first several isotherms. Both phase transitions gradually disappear with time as noted in the later isotherms. Note that, in this sense, “condensed” refers to the physical packing of the amphiphiles rather than the chemical bonding of the headgroups.

The inset of Figure 1 shows an expanded view of the isotherm behavior in the LE–LC transition region. In this transition region isotherms 2–4 are displaced $\sim 6 \text{ \AA}^2/\text{molecule}$ to the right (to greater molecular areas) of isotherm 1. After the fourth isotherm (3 h after the reaction started) it is noted that the isotherms begin to shift to the left, or lower molecular areas. After 23 h a limiting area per molecule of $22 \text{ \AA}^2/\text{molecule}$ (isotherm 30) has been reached, thereby indicating hydrolysis completion. The completion of condensation was verified by fluorescence images of transferred films stained with Rh–Fer as described later. Below the LE–LC transition region, successive isotherms shift to lower molecular areas at all times. Above the LE–LC transition regions, the behavior is somewhat complicated. Between 13 and 20 mN/m, the isotherms shift to lower molecular areas at all times. However, between 20 and 30 mN/m, the isotherms first shift to greater molecular areas and then toward lower molecular areas.

Monolayer Packing Density and OTMS Reactivity—Figure 2 shows $A(t)$ isobars for OTMS on H_2O , pH 5.6. The monolayers were held at surface pressures of 5, 10, 15, 20, and 25 mN/m after 10 min incubation times ($t_0 = 10 \text{ min}$) at zero surface pressure. These $A(t)$ isobars reproduce the general behavior demonstrated by the isotherms in Figure 1; however, only the 5, 10, and 15 mN/m isobars converge to a limiting area of $22 \text{ \AA}^2/\text{molecule}$ within 18 h after monolayer spreading. The $3 \text{ \AA}^2/\text{molecule}$ increase in molecular area during the first 1.5 h for the 10 mN/m isobar may be attributed to electrostatic repulsion and/or packing restrictions among reaction intermediates as discussed later.

As a means of verifying extent of reaction, successive π – A isotherms of the monolayers were measured after the $A(t)$ experiments. For the films held at 5, 10, and 15 mN/m, the π – A isotherms were identical to isotherm 30 in Figure 1, indicating reaction completion. To the contrary the π – A isotherms measured for the films held at 20 and 25 mN/m for 24 h reproduced isotherm 1 in Figure 1. Furthermore, the successive isotherms measured for the films held at 20 and 25 mN/m reproduced isotherms 2–30 shown in Figure 1.

Isoarea vs Isobaric Conditions—Figure 3 compares an OTMS monolayer held under isobaric conditions ($A(t)_{\pi=10 \text{ mN/m}}$) with an OTMS monolayer held under isoarea conditions ($\pi(t)_{A=36 \text{ \AA}^2/\text{molecule}}$). The subphase was H_2O , pH 5.6, and the incubation time at zero surface pressure (t_0) was zero for both monolayers. The $A(t)_{\pi=10 \text{ mN/m}}$ isobar in Figure 3 displays an initial $2.5 \text{ \AA}^2/\text{molecule}$ increase in molecular area, followed by a shoulder (between hours 9 and 12) centered near $33 \text{ \AA}^2/\text{molecule}$. After this the slope again increases (hours 12–19) before eventually leveling off, reaching a limiting area of $22 \text{ \AA}^2/\text{molecule}$ after 30 h. A π – A isotherm of this film (not shown) confirmed reaction completion.

The $\pi(t)_{A=36 \text{ \AA}^2/\text{molecule}}$ isoarea kinetics curve in Figure 3 displays an initial 0.5 mN/m increase in surface pressure, followed by a plateau region (between hours 9 and 12) of approximately zero slope. Between hours 12 and 16, the surface pressure drops very rapidly to zero. A π – A isotherm (not shown) resembling isotherm 30 in Figure 1 confirmed reaction completion and indicated that a limiting molecular area of $22 \text{ \AA}^2/\text{molecule}$ was also reached under the given isoarea conditions. Arrows indicating characteristic curve maxima and inflection points have been placed on the $A(t)$ and $\pi(t)$ kinetics curves to facilitate comparison.

Effects of Monolayer Incubation Time at Zero Surface Pressure (t_0)—The dependence of the 10 mN/m isobar shape on t_0 is evident in comparing Figure 2 ($t_0 = 10$ min) with Figure 3 ($t_0 = 0$). This dependence is further demonstrated in the $A(t)$ isobars ($\pi = 10$ mN/m) presented in Figure 4 in which t_0 was varied between 0 and 60 min. A PBS, pH 4.3 subphase was used to accelerate the hydrolysis and condensation reactions.

An initial molecular area increase of $2.5 \text{ \AA}^2/\text{molecule}$ is observed for the $t_0 = 0$ $A(t)$ isobar in Figure 4. This initial area increase is followed by a short plateau region over which the molecular area remains constant at $33 \text{ \AA}^2/\text{molecule}$ for ~ 1 h. After this plateau the molecular area again decreases, approaching a limiting molecular area of $22 \text{ \AA}^2/\text{molecule}$ within 8 h after the monolayer was spread. For the $t_0 = 10$ min $A(t)$ isobar, an initial peak in molecular area is also observed; however, this molecular area increase is only $\sim 1 \text{ \AA}^2/\text{molecule}$. This peak is followed by a second molecular area increase ($\sim 0.5 \text{ \AA}^2/\text{molecule}$) centered near $32.5 \text{ \AA}^2/\text{molecule}$. After this second increase the molecular area again decreases, approaching the limiting molecular area of $22 \text{ \AA}^2/\text{molecule}$. The $t_0 = 25, 35$, and 60 min $A(t)$ isobars do not display the initial molecular area increase observed for the $t_0 = 0$ and 10 min isobars. However, the $t_0 = 25$ and 35 min isobars display shoulder regions centered near $33 \text{ \AA}^2/\text{molecule}$ over which the molecular area decrease is diminished for ~ 1 h. The π - A isotherms (not shown) measured after the isobar experiments on these monolayers confirmed reaction completion.

II. Monofunctional Silane Kinetics

OMMS π - A Isotherms—Figure 5 presents a series of consecutive OMMS π - A isotherms recorded over 4.5 h on a PBS, pH 4.3 subphase, $t_0 = 10$ min. The average elapsed time between isotherms was 9 min. As with OTMS the monofunctional OMMS also undergoes an LE-LC phase transition. However, this transition is centered at 7 mN/m for OMMS, compared to 11 mN/m for OTMS (see Figure 1). An LC-SC phase transition is not observed for OMMS. Similar to OTMS, the OMMS isotherms also initially shift to greater molecular areas in the LE-LC region. A limiting molecular area of $16 \text{ \AA}^2/\text{molecule}$ was attained after 4.5 h, after which time no further change in isotherm shape or position was noted.

Mono- vs Trifunctional Silane Kinetics—Figure 6 compares $A(t)$ isobars for OMMS ($\pi = 6$ mN/m) and OTMS ($\pi = 10$ mN/m) on PBS pH 4.3, $t_0 = 0$. It is appropriate to compare OTMS $\pi = 10$ mN/m isobars with OMMS $\pi = 6$ mN/m isobars because at these surface pressures both silanes have just entered their respective LE-LC phase coexistence regions (compare Figure 1 with Figure 5). The isobars in Figure 6 show that the rate of molecular area increase is about the same for both OTMS and OMMS; however, the rate of molecular area decrease is much reduced for OMMS, requiring 24 h to reach a limiting area of $19 \text{ \AA}^2/\text{molecule}$.

III. OTMS Chemical Condensation

Monolayer Transfer—Fluorescence images of the horizontally transferred OTMS monolayers suggest that the monolayers were transferred intact (i.e. transfer ratio = 1), except at the edges of the hydrophobic coverslips. The OTMS headgroups were believed to

be oriented toward the ambient as the coverslips appeared very hydrophilic after monolayer transfer and did not readily dewet if removed from the fluid cell.

OTMS Chemical Condensation and OTMS Physical Phases—Figure 7 shows fluorescence images of OTMS monolayers prepared on H₂O, pH 5.6, $t_0 = 0$, compressed and held at 10 mN/m for 3 h, and then horizontally transferred and stained with Rh–Fer. With reference to the 10 mN/m isobar in Figure 3, it is seen that under these conditions the molecular area increase is at a maximum value near the 3 h mark. As shown in Figure 7A, the monolayer was primarily composed of 15–25 μm gray circular domains. Occasionally, large dark structures (Figure 7B) were observed within these gray domains; however, these were the rare exception. Monolayers transferred after 24 h at 10 mN/m were composed primarily of 15–25 μm hexagonal and star-shaped domains as shown in Figure 8A. In contrast monolayers transferred after 24 h at surface pressures of 15 and 19 mN/m (Figure 8B,C, respectively) were composed of 15–50 μm circular (Figure 8B) and 15–100 μm distorted circular (Figure 8C) domains.

Monolayers prepared at surface pressures higher than 20 mN/m demonstrated a coalescence of the LC domains to form a continuous matrix as indicated in Figure 9A. The monolayer in Figure 9A was transferred after 5 h at 25 mN/m and then stained with Rh–Fer. The small bright domains are regions of enhanced Rh–Fer binding, which may correspond to entrapped LE or LC phases within the SC matrix. Figure 9B is a fluorescence image of a monolayer prepared under identical conditions but transferred after 24 h at 25 mN/m and then stained. The small circular domains, preferentially stained in Figure 9A, now appear black. It is also noted that the SC matrix is nonuniformly stained by Rh–Fer.

Discussion

Protonation and Hydrolysis

As shown in Figure 1, OTMS π –A isotherms display features indicative of the chemical and physical properties of the monolayer. The plateau near 11 mN/m corresponds to a liquid expanded to condensed (LE–LC) phase transition while the plateau at 20 mN/m has been attributed to an undulation effect.⁷ This effect is also referred to as a liquid condensed to solid condensed (LC–SC) phase transition in which adjacent methoxy groups assume a staggered conformation. The disappearance of these plateaus with time is an indication that methoxy groups are being replaced with hydroxy groups. Thus, changes in isotherm shape can be used to monitor extent of hydrolysis. Monitoring the extent of reaction through successive π –A isotherms has the advantage that it samples a range of surface pressures; however, it also has the disadvantage in that it further complicates the analysis since both molecular area and surface pressure are variable.

The $A(t)$ and π –A kinetics behaviors presented for both OTMS and OMMS monolayers suggest that the molecules are protonated preceding hydrolysis. While the formation of cyclic or branched oligomers, which do not pack as efficiently as monomers, could also explain the area increases observed for OTMS,¹⁰ this cannot be the case for OMMS which can only form dimers. An alternative explanation is that the area increases for both OTMS and OMMS films results from steric interactions associated with dimerization.¹¹ The dimers

may initially be in high molecular area gauche configurations, which later assume the lower molecular area, trans-configurations where the alkyl chains are normal to the interface. However, given the high polarity of the air/water interface, the gauche conformation is energetically unfavorable as it places the alkyl tails closer to the aqueous subphase. Thus, the displacement of π - A isotherms to larger areas and the observed increases in surface pressure or molecular area (including the $A(t)$ experiments) are attributed to the formation of charged OTMS molecules.

The OTMS and OMMS π - A isotherms (Figures 1 and 5) demonstrated that the molecular area increase is most evident when the monolayers are in their respective LE-LC transition regions. For this reason we chose to monitor OTMS and OMMS hydrolysis at $\pi = 10$ and $\pi = 6$ mN/m, respectively. At $\pi = 10$ mN/m, OTMS had an initial area of ~ 35 – 36 Å²/molecule on H₂O, pH 5.6, subphases (Figures 2 and 3). On PBS, pH 4.3 (150 mM ionic strength), subphases, the initial OTMS molecular area was ~ 33 Å²/molecule (Figure 4). This contraction of the monolayer on the PBS subphases further suggests that OTMS is charged immediately after spreading. Sjöblom and co-workers demonstrated that OTMS and OMMS films contracted by 3.6 and 6.3 Å²/molecule in their LE-LC coexistence regions on 10 mM CaCl₂ subphases, pH 5.6.³ Their results also suggest an electrostatic basis for the molecular area increases as reported here.

On the basis of these observations, we propose the hydrolysis of the first methoxy group on OTMS occurs as follows on acidic subphases:

where R represents the octadecyl chain and R represents a methyl group. Reaction 1 depicts the electrophilic process of protonation of a methoxy group on OTMS. Once protonated, the nucleophilic attack of water on the silicon atom of OTMS readily occurs as shown in reaction 2. Alkoxy moieties are poor leaving groups, however, the protonated alkoxy moiety is a much better leaving group.^{5,12} Protonation of alkoxy groups prior to hydrolysis is known to occur in bulk sol-gel processes^{5,13–15} and may be similarly expected to occur at the air/water interface. Once an OTMS molecule is monohydrolyzed (reaction 2), it may either undergo further protonation and hydrolysis or it may participate in chemical condensation:

These reactions depict the alcohol and water producing chemical condensation reactions. Although it is not indicated in eq 3, it is likely that an alkoxy group is also protonated prior to alcohol producing condensation. Due to the high probability of OTMS-OTMS collisions for molecules confined to an interface, condensation is expected to follow hydrolysis.^{1,2,8}

If each methoxy group on OTMS has a unique protonation and hydrolysis rate,^{4,5} then it may be expected that discrete protonation and hydrolysis events are discernible in the reaction kinetics. The plateau and shoulder regions (Figures 3 and 4) observed following the initial peaks in molecular area suggest that either the rate of area-reducing reactions (hydrolysis/condensation) has decreased or the rate of area-increasing reactions (protonation) has become enhanced. Since in some instances the “plateau” region was actually a molecular area increase (Figure 4, $t_0 = 10$), we hypothesize that this corresponds to the protonation of a second methoxy group.

Why the second protonation event does not lead to the large area increase seen for the first protonation event may be a manifestation of a decreased lifetime of the protonated dimethoxy intermediate ($\text{C}_{18}\text{Si}(\text{OH})(\text{OCH}_3)(\text{OCH}_4)^+$) relative to protonated trimethoxy intermediate ($\text{C}_{18}\text{Si}(\text{OCH}_3)_2(\text{OCH}_4)^+$). As methoxy groups are replaced by hydroxy groups on a given OTMS molecule, the protonation rate for the remaining methoxy groups *decreases*, while the hydrolysis rate of these protonated methoxy groups *increases*.⁵ Since both the rate at which protonated species are formed and the lifetimes of these intermediates decrease with each methoxy group, it is not surprising that the second protonation event is diminished relative to the first, and the third protonation event is unobserved.

Sensitivity and Detection of Reaction Intermediates

Protonation of OTMS monomers and oligomers may lead to electrostatic repulsion among the like charges on these intermediates. This protonation leads to the observed molecular area increases. In addition to electrostatic repulsion, geometric constraints on the monolayer may arise from the pentacoordinate bonding at the silicon atom of the intermediates.^{15–17} Whether these reaction intermediates are actually detected using surface pressure techniques depends on the number of charged species present, their lifetimes, distribution within the monolayer, and lateral diffusivity.

As shown in Figure 3, both the $A(t)$ and $\pi(t)$ methods are sensitive to OTMS protonation and hydrolysis. Although, the shapes of these two curves differ considerably, the characteristic “peak/plateau” features, i.e., curve maxima and inflection points (indicated by arrows), occur at approximately the same times under $A(t)$ and $\pi(t)$ conditions. Maintaining a constant surface pressure ($A(t)_{\pi=\text{const}}$) appears advantageous since it ensures that the monolayer packing density is maintained proportional to amphiphile size throughout the course of the reaction. The importance of this experimental condition is 2-fold: First, OTMS monolayer reactivity depends on the conformational mobility and lability of reactants to the electrophilic and nucleophilic processes of protonation and hydrolysis, respectively. This influence of monolayer packing density is also evident in Figure 2 in which OTMS monolayers held above 20 mN/m were unreactive. Second, the sensitivity of surface pressure techniques to changes in molecule size also depends on the packing density of the molecules. Highest sensitivity is achieved when the monolayer packing density is such that the average area *available* per molecule matches the *actual* molecular area of the amphiphile. For OTMS and OMMS this requirement corresponds to holding the monolayers in their respective LE–LC transition regions.

OTMS Chemical Condensation and OTMS Physical Phases

Figure 7A demonstrates that OTMS films transferred from H₂O, pH 5.6, subphases during the peak in molecular area are composed primarily of 15–25 μm sized circular domains. These domains correspond to LC phases separated by an LE phase. The large dark structures occasionally observed within the LC phases (Figure 7B) are likely chemically condensed (CC) domains. The two similar sized hexagonal chemically condensed domains in Figure 7B appear to be the result of a highly ordered growth mechanism and not a random diffusion and aggregation process of OTMS molecules. Although the fluorescence image in Figure 7B suggests that chemical condensation is enhanced in the LC phase, the kinetics data (Figure 2) indicate that hydrolysis in monolayers held at various LE:LC ratios ($\pi = 5, 10, 15 \text{ mN/m}$) reaches completion in approximately the same time. Whether the close proximity of the OTMS molecules in the LC phases accelerates condensation is uncertain.

Once hydrolysis and condensation is complete under isobaric conditions of 10 mN/m, the chemically condensed domains clearly display 6-fold symmetry (Figure 8A). In contrast, monolayers prepared at 15 mN/m for 24 h display circular chemically condensed domains (Figure 8B). Monolayers prepared at the upper end of the LE–LC coexistence region (19 mN/m) for 24 h display closely packed, distorted circular domains (Figure 8C). The arrow in Figure 8C indicates where a domain has fractured. When the surface pressure is raised above 10 mN/m, the star and hexagonal chemically condensed domain are absent (Figure 8B,C) suggesting that their growth mechanism requires the OTMS molecules to be relatively unconstrained and laterally mobile. At higher surface pressures (i.e. 15 mN/m), the chemically condensed domain morphology appears to be restricted to the circular shapes of the LC phases. As the surface pressure is raised beyond the LC–SC transition point (20 mN/m), OTMS hydrolysis and chemical condensation are sterically restricted.

This diminished reactivity of monolayers prepared at 25 mN/m is illustrated in Figure 9. When the monolayer is kept at 25 mN/m for 5 h, negatively charged Rh–Fer binds to the small LE/LC phases entrapped with SC matrix (Figure 9A). If, however, the monolayer is kept at the same surface pressure for 24 h, then the Rh–Fer binding to the entrapped domains is absent (Figure 9B). The effect of monolayer incubation time on Rh–Fer binding suggests that these entrapped domains undergo a reversal of charge from positive to negative as protonation, hydrolysis, and condensation proceed. The charge reversal is in agreement with surface potential studies of transferred OTMS monolayers⁷ and indicates that Rh–Fer binding to the transferred monolayers is based on Coulombic interactions as well as possible monolayer packing density effects.

In light of potential differences in OTMS reactivity in the LE vs LC phases, it is tempting to ascribe the peak, plateau, and shoulder features in the $A(t)$ and $\pi(t)$ kinetics to differences in reaction rates in these two phases rather than to a stepwise reactivity of methoxy groups. However, we feel the latter explanation provides a more accurate picture of the kinetics for several reasons. First, as previously mentioned, monolayers held at various LE:LC ratios reach completion in approximately the same time. Thus, a large difference in reaction rates between the LE and LC phases appears unlikely. Second, at 15 mN/m OTMS is predominantly in an LC phase, yet the 15 mN/m isobar in Figure 2 does not show a

molecular area increase like the 10 mN/m isobar. If the initial peak in molecular area were due to faster kinetics in the LC phase, then one would expect to see an initial molecular area increase in monolayers held at 15 mN/m. However, for the 5 mN/m isobar in which OTMS is primarily in an LE phase, the characteristic features ascribed to protonation are evident. The features attainable in the 5 mN/m kinetics isobar are limited by a decreased sensitivity of the surface balance and increased diffusivity of OTMS at this lower packing density (see previous discussion on sensitivity).

Additional support for the hypothesis that the peak/plateau features result from stepwise protonation and hydrolysis kinetics and not from differences in protonation and hydrolysis in the LE and LC phases is found in the OMMS reaction kinetics (Figure 6). OMMS is also held in its LE–LC coexistence region ($\pi = 6$ mN/m), but only a single molecular area increase event is observed. We attribute this increase to protonation of the single methoxy group on OMMS molecules in the LE phase. If the reaction rates in the LE and LC phases were significantly different, then distinct peak/plateau features would be expected for OMMS.

The increased lifetime of the protonated OMMS relative to OTMS (Figure 6) is attributed to the increased organic substitution around the OMMS silicon atom, which stabilizes the protonated intermediate.¹² This increased lifetime is also a manifestation of a decreased hydrolysis rate of the protonated OMMS intermediate at $\pi = 6$ mN/m. In contrast, the protonated intermediates formed in OMMS monolayers cycled between 0 and 25 mN/m (Figure 5) appear to be more readily hydrolyzed. These results suggest that, when OTMS and OMMS monolayers are held at fixed surface pressures in their respective LE–LC coexistence regions, the rate-limiting reaction is the nucleophilic attack of water on the protonated species rather than the electrophilic process of protonation.

Conclusions

The hydrolysis kinetics of octadecyltrimethoxysilane (OTMS) and octadecyldimethylmethoxysilane (OMMS) at the air/water interface were investigated using a Langmuir trough. Monitoring the films' compression into their respective LE–LC coexistence regions immediately after spreading allowed for the detection of molecular area increases attributed to protonated reaction intermediates. For OTMS these area increases were observed at discrete intervals which were attributed to the stepwise protonation and hydrolysis of methoxy groups on this trifunctional silane. The observation of only a single molecular area increase event for monofunctional OMMS further supports this hypothesis. Analogous to bulk sol–gel reactions, the interfacial silane kinetics indicated that methoxy-group protonation occurred rapidly and hydrolysis was rate determining. For OTMS films held at or above surface pressures of 20 mN/m, hydrolysis was inhibited, presumably due to steric influences on the chemical reactivity of silanes confined at the interface. These results demonstrate that the Langmuir trough not only provides a convenient means for monitoring silane assembly kinetics but also a means to directly control reaction rates and condensed domain morphology through monolayer packing density.

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References

1. Lindén M, Slotte JP, Rosenholm JB. *Langmuir*. 1996; 12:4449.
2. Fontaine, P.; Rondelez, F. Kinetics of polymerisation in Langmuir monolayers of *n*-alkyltrimethoxysilane. In: Daillant, J., editor. *Short and Long Chains at Interfaces*. France: Editions Frontieres: Gif-sur-Yvette Cedex; 1995. p. 207
3. Sjöblom J, Stakkestad G, Ebeltoft H, Friberg SE, Claesson P. *Langmuir*. 1995; 11:2652.
4. Sefcák J, McCormick AV. *Catal. Today*. 1997; 35:205.
5. Sanchez J, McCormick A. *J. Phys. Chem.* 1992; 96:8973.
6. Fang J, Knobler CM. *J. Phys. Chem.* 1995; 99:10425.
7. Taylor DM, Gupta SK, Dynarowicz P. *Thin Solid Films*. 1996; 284–285:80.
8. Britt DW, Hlady V. *J. Phys. Chem. B*. Submitted.
9. Britt DW, Hlady V. *J. Colloid Interface Sci.* 1996; 178:775. [PubMed: 25125702]
10. Ariga K, Okahata Y. *J. Am. Chem. Soc.* 1989; 111:5618.
11. Sjöblom J, Ebeltoft H, Bjørseth A, Friberg SE, Brancewicz C. *J. Disp. Sci. Technol.* 1994; 15:21.
12. Arkles, B.; Steinmetz, JR.; Zazyczny, J.; Mehta, P. Factors contributing to the stability of alkoxysilanes in aqueous solution. In: Anderson, R.; Larson, GL.; Smith, C., editors. *Silicon Compounds: Register and Review*. Piscataway, NJ: Hüls America Inc.; 1991. p. 301
13. Buckley AM, Greenblatt M. *J. Chem. Educ.* 1994; 71:559.
14. Chen SL, Dong P, Yang GH, Yang JJ. *Ind. Eng. Chem. Res.* 1996; 35:4487.
15. Osterholtz FD, Pohl ER. *J. Adhes. Sci. Technol.* 1992; 6:127.
16. Sugahara Y, Tsuyoshi I, Kuroda K. *J. Mater. Chem.* 1997; 7:53.
17. Brinker, DJ.; Scherer, GW. *Sol–Gel Science*. San Diego, CA: Academic Press; 1990.

Figure 1.

OTMS surface pressure vs molecular area isotherms on H₂O, pH 5.6, $t_0 = 10$ min. The time between isotherms is 46 min, and numbers on isotherms indicate order in which they were attained. The inset shows an expanded view of the isotherm behavior in the LE-LC coexistence region ($\pi = 8\text{--}12$ mN/m). Note that isotherms 2–4 (thick curves) shift to greater molecular areas. Isotherms 5–30 shift to lower molecular areas, reaching a limiting area of $22 \text{ \AA}^2/\text{molecule}$ after 23 h.

Figure 2.

OTMS molecular area vs time isobars on H_2O , pH 5.6. After 10 min incubation times at zero surface pressure, the monolayers were compressed to the indicated feedback surface pressures of 5, 10, 15, 20, or 25 mN/m.

Figure 3.

Comparison of OTMS monolayers held under isobaric and isoarea conditions on H_2O , pH 5.6, $t_0 = 0$ for each. The arrows indicate characteristic curve maxima and inflection points. A limiting molecular area of $22\text{\AA}^2/\text{molecule}$ was reached within 30 h for the monolayer held under isobaric conditions.

Figure 4.

OTMS molecular area vs time isobars ($\pi = 10$ mN/m) on PBS, pH 4.3. The monolayer incubation time at zero surface pressure (t_0) is indicated next to each isobar. Isobars are displaced from each other by 2 h for clarity.

Figure 5.

OMMS surface pressure vs molecular area isotherms on PBS, pH 4.3, $t_0 = 10$ min. The time between isotherms is 9 min, and numbers on isotherms indicate the order in which they were attained. The inset shows an expanded view of the isotherm behavior in the LE-LC coexistence region ($\pi = 5\text{--}9$ mN/m). Note the displacement of isotherms 2 and 3 to greater molecular areas in the LE-LC region. Isotherms 4–30 shift to lower molecular areas, reaching a limiting area of $16\text{Å}^2/\text{molecule}$ after 4.5 h.

Figure 6. OTMS and OMMS isobars (10 and 6 mN/m, respectively) on PBS, pH 4.3, $t_0 = 0$.

Figure 7. Fluorescence images of OTMS monolayers prepared on an H₂O, pH 5.6, subphase, $t_0 = 0$, and then held at 10 mN/m for 3 h before transfer for staining and analysis: (A) typical image of OTMS physical phases (LE, LC); (B) chemically condensed (CC) structures forming in the LC phase (see text for discussion).

Figure 8.

Fluorescence images of OTMS monolayers prepared on an H_2O , pH 5.6, subphase, $t_0 = 0$, and then held at either 10, 15, or 19 mN/m (A–C, respectively) for 24 h before transfer for staining and analysis: (A) chemically condensed domains displaying 6-fold symmetry; (B) chemically condensed domains displaying circular morphologies; (C) chemically condensed domains displaying distorted circular morphologies. The arrow indicates a fractured domain.

Figure 9. Fluorescence images of OTMS monolayers prepared on an H_2O , pH 5.6, subphase, $t_0 = 0$, and then held at 25 mN/m for 5 h (A) and 24 h (B) before transfer for staining and analysis: (A) enhanced Rh–Fer binding to small domains (LE/LC phases) entrapped within a close-packed SC phase matrix; (B) chemical condensation (CC) of the OTMS in the entrapped LE/LC domains is manifested by a diminished Rh–Fer binding.