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Two-Dimensional Gelation: Octadecyltrimethoxysilane at the Air/Water Interface

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Hydrolysis and condensation of spread monolayers of octadecyltrimethoxysilane (ODTMS) have been studied as a function of pH by means of in-situ epifluorescence microscopy, surface potential and compression isotherms within the pH range 0.5–13.5. The point of zero charge of the monolayer was found to be 3. At pH < 3 the ODTMS monolayer was positively charged whereas it was negatively charged at pH > 12. The hydrolysis was both acid and base catalyzed. Unlike what has been observed for corresponding three-dimensional sol-gel reactions, condensation occurred immediately after the methoxy groups had hydrolyzed, as evidenced by fluorescence microscopy. Large continuous aggregates of condensed ODTMS were observed if the monolayer was allowed to undergo surface pressure relaxation at constant area. The time required before gelation was observed varied between a couple of minutes at extreme pH values to 10 h at intermediate pH. Depending on the pH, floc-like or gel-like structures were formed.

Introduction

The high molecular order obtainable in organic mono- and multilayer films by using the Langmuir–Blodgett (LB) technique makes it an ideal tool for the investigation of two-dimensional polymerization reactions involving water insoluble monomers.^{1–6} In most of the previous studies the polymerizable group has been situated in the hydrocarbon part of the surfactant. Recently, however, the polymerization of different derivatives of alkylsilanes at the air/water interface with various possible condensation levels and different numbers of hydrocarbon chains has been reported.^{7–10} The polymerization reaction consists of two steps: (i) the hydrolysis of the polar silane head group and (ii) the subsequent formation of Si–O–Si bonds between adjacent head groups. These reactions have found much use in the solution–gelation (sol-gel) procedure applied in the preparation of e.g. glass ceramics, typically using tetramethoxysilane (TMOS) or tetraethoxysilane (TEOS) as precursors. In self-assembly processes chlorosilanes are usually used. However, methoxy- or ethoxysilanes are more suitable for studies on polymerization kinetics, since these are more stable with respect to hydrolysis.¹¹ It is well-known that the hydrolysis step is strongly pH-dependent. In three-dimensional reactions the rate of hydrolysis is highest at extreme pH values, since it is specifically catalyzed by

both H⁺ and OH[−] ions.¹² This has also been shown to be the case for the hydrolysis of monolayers of alkylmethoxy- and alkylethoxysilanes spread at the air/water interface.^{8,9} However, it has been suggested that the lower freedom of movement in the monolayer compared to in the bulk and geometrical restrictions concerning the in-plane monolayer packing make it difficult to transfer knowledge from bulk reactions directly to the two-dimensional case.⁹ In this work we have investigated the polymerization of spread monolayers of octadecyltrimethoxysilane (ODTMS) as a function of pH in the pH region 0.5–13.5 by measuring standard surface pressure/surface potential isotherms and by in-situ fluorescence microscopy. The aim of the study was to investigate the possibility of using well defined two-dimensional systems in order to obtain information about the aggregation processes leading to the formation of gels and particles in the sol-gel process.

Experimental Details

Materials. Octadecyltrimethoxysilane (ODTMS, 90% purity), *n*-hexane (99%), and chloroform used as the spreading solvent were supplied by Fluka Chemicals. ³¹Si-NMR was performed on the ODTMS sample to ensure that no prehydrolysis had occurred before spreading of the monolayer. Dilute solutions of HCl and NaOH were used to adjust the pH. BODIPY–hexadecanoic acid (Molecular Probes Inc.) was used as the fluorescent probe (1.2 mol %). All chemicals were used as supplied. The distilled water was purified with a Millipore Milli-Q filtering system with two carbon and two ion-exchange stages and finally a filtration through a 0.22-μm Zetapore filter, yielding a water resistivity > 18 MΩ cm^{−1}. The pH of the pure water was 5.7 and was determined by dissolved CO₂.

Monolayer Formation. The experimental setup used for measuring the compression and surface potential isotherms has been described earlier.¹³ The compression was started 10 min after spreading, if not otherwise mentioned, at a constant barrier speed of 2.5 Å²/(molecule·min). The fluorescence microscopy measurements were carried out using a two-barrier, symmetrical compression KSV minitrough (KSV Instruments, Helsinki, Finland) equipped with a Hitachi video camera connected to a DT3851 digitizing board (Data Translation, Marlboro, MA). During the epifluorescence microscopy measurements a compression speed of 1 Å²/(molecule·min) was used. Surface textures

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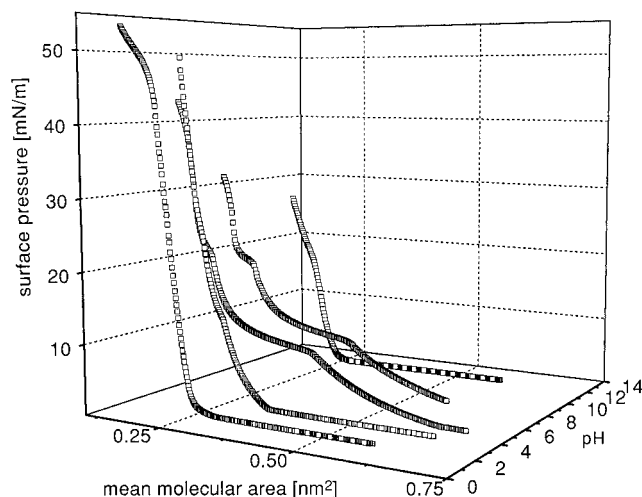


Figure 1. Compression isotherms of ODTMS in pure water as a function of pH.

are observed due to the much lower solubility of the probe in condensed compared to fluid phases.

Results

Compression Isotherms. The compression isotherms of ODTMS at different pH values are shown in Figure 1. As expected, the compression isotherms were very sensitive to changes in pH. At intermediate pH values the monolayer passed through both the liquid expanded (LE) and the liquid condensed (LC) states, with a LE–LC transition pressure, π_{tr} , of about 9 mN/m. Highly condensed monolayers with only one clear transition to the LC state were observed in both the low- and high-pH regions. The mean molecular area where the first increase in surface pressure was observed, A_i , was 0.7 nm² at neutral pH and was clearly determined by the large size of the polar head group. The A_i value decreased to about 0.25 nm² for the condensed monolayers. The isotherms observed in the first case resembled the surface pressure isotherms of many lipids and fatty acids possessing *trans* unsaturation. However, the additional plateau in the isotherm of ODTMS at 19 mN/m corresponding to the transition from the LC state to the condensed state is normally not seen for other film-forming substances. The transition pressures observed here for ODTMS at intermediate pH values differ greatly from corresponding pressures reported in a previous investigation by another group,⁹ ≈ 30 and 55 mN/m. However, the values we report here were obtained using several different surface balances and different compression speeds. We believe that the pressure values previously reported are too high, especially since they report surface pressures exceeding 100 mN/m in the condensed state at other pH values. The initial surface pressure after spreading (to mean molecular areas of typically 0.60 nm²) decreased rapidly from about 2.5 mN/m to close to zero within a couple of minutes at pH values where fully condensed monolayers were observed. The final extrapolated molecular area in the most condensed state was 0.195 nm² at intermediate pH, which indicates that the molecular area observed in the most condensed state was determined by the hydrocarbon chain at these pH values. For the fully condensed monolayers the corresponding molecular area increased gradually to reach 0.23–0.25 nm². However, the mean molecular area concept does not have any real physical significance, due to aggregation into large aggregates and eventually two-dimensional gels, as shown later. The fully condensed monolayers were very rigid, and the Wilhelmy plate was eventually pushed along with the monolayer at high

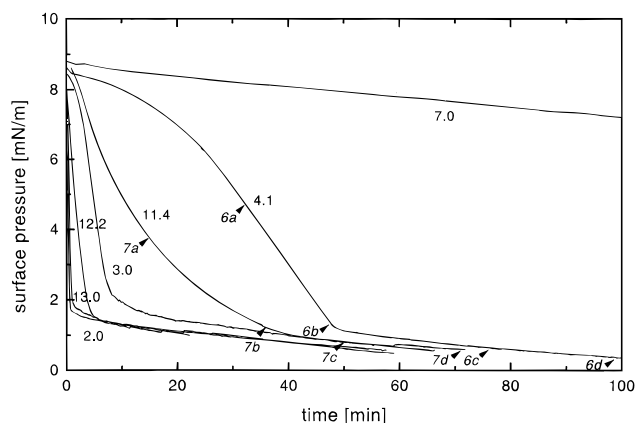


Figure 2. Surface pressure relaxation of ODTMS at a constant mean molecular area of 0.50 nm² obtained at the pH values indicated in the figure. 6a–d and 7a–d refer to Figures 6 and 7, respectively.

surface pressures when asymmetric compression was used, introducing errors in the measured surface pressure values in this region. In the pH intervals 3.5–5 and 10.5–12 the compression isotherms were intermediate between the condensed and expanded type isotherms, possessing some LE state properties.

Surface Pressure Relaxation at Constant Area.

Surface pressure relaxation measurements of monolayers spread to a constant area of 0.50 nm² were carried out as a function of time after spreading. Measurement of the monolayer area relaxation at constant surface pressure would appear more suitable for this kind of study,¹⁴ but since the aggregation processes taking place in the ODTMS monolayer occurred at a very fast rate at low and high pH, extensive hydrolysis/condensation would have taken place before reaching the target surface pressure. Furthermore, spreading to a mean molecular area of 0.50 nm² should ensure that the surfactant molecules have enough free space to arrange into a low-energy conformation. Therefore surface pressure relaxation at constant area was regarded as more suitable. It must be remembered, however, that the spreading solvent might influence the observed surface pressure relaxation during the first minutes after spreading, even though we do not believe that this effect had any major influence on the measured relaxation curves. The observed surface pressure at $t = 0$ was generally about 8 mN/m. However, at low- and high-pH values slightly lower surface pressures were observed, indicating that partial hydrolysis of the methoxy groups had taken place instantaneously after spreading. The relaxation curves generally consisted of three different regions. Initially a slow decrease in surface pressure with time was observed followed by a region of faster decay. Finally a region with almost constant surface pressure of 0.5–1 mN/m was observed. The shape of the surface pressure relaxation curves was very similar to that of the recently reported area relaxation curves for the same system.¹⁵

The surface pressure decay with time showed a dramatic dependence on pH, as shown in Figure 2. At pH = 7 the surface pressure relaxation was very slow and the plateau value was observed after about 600 min. In the low- and high-pH regions the relaxation times were radically shortened. At pH = 2 and pH = 13 the plateau value was reached within a couple of minutes after spreading. The surface pressure relaxation followed nicely the observed

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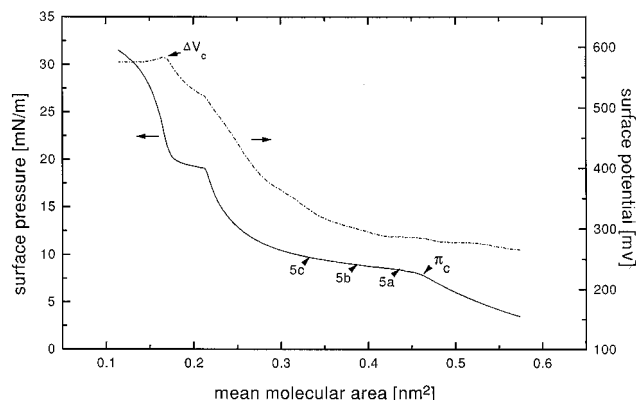


Figure 3. Compression and surface potential isotherms of a ODTMS monolayer at pH = 10.6 5a–c refer to Figure 5.

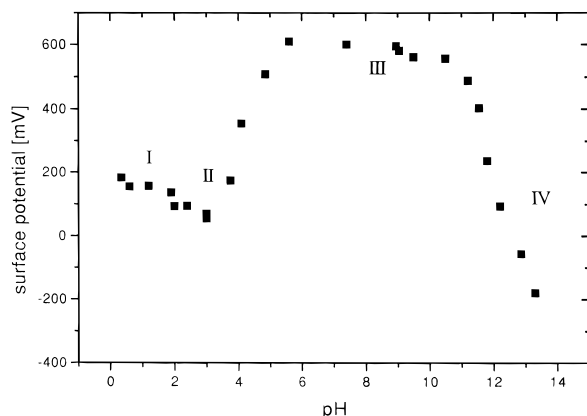


Figure 4. ΔV_c vs pH for ODTMS monolayers in a pure water subphase. Regions I–IV are referred to in the Discussion.

pH dependence of the compression isotherms and of the ΔV_c data (see later).

Surface Potential Isotherms. The surface potential, ΔV , of the monolayer was measured simultaneously with the surface pressure during compression. The $\Delta V/A$ isotherms followed nicely the changes in the compression isotherm and were reproducible over the whole area range studied. A typical $\Delta V/A$ isotherm measured at pH = 10.6 is shown in Figure 3. A sharp increase in ΔV from around 0 mV to about 250 mV occurred at areas corresponding to the transition from the G–LE coexistence region to the LE state at this pH. Upon further compression another continuous increase in ΔV was observed between about 0.45 and 0.20 nm² until a value of 600 ± 15 mV was observed when the monolayer had reached the condensed state. At pH < 3.5 the ΔV isotherm resembled the isotherms observed for saturated fatty acids with an almost constant value of about 0 mV during compression until a mean molecular area of 0.35 nm² was reached. Here a sharp increase in ΔV was observed, and depending on the pH, a maximum between 60 and 200 mV was observed in the condensed state. The ΔV value observed in the condensed state, denoted ΔV_c (see Figure 3), was chosen as the value of comparison between different experimental conditions and is shown in Figure 4. At pH = 0.5 a value of 200 mV was observed, which gradually decreased with increasing pH to reach a local minimum of about 70 mV at pH = 3. A sharp increase in ΔV_c occurred between pH = 3 and 5.5 to finally reach a plateau value of about 600 mV. At pH = 10.7 a continuous decrease in ΔV_c was observed to values close to those observed in the low-pH region. However, the continuous decrease in ΔV_c , eventually to negative values, indicated that the monolayer became negatively charged at high pH.

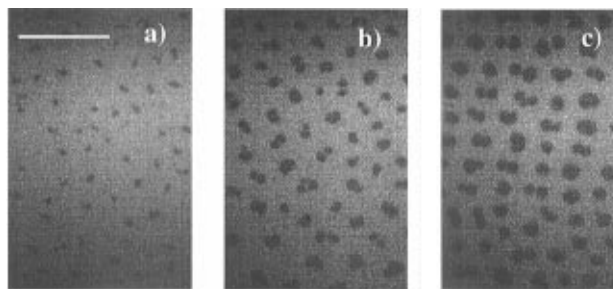


Figure 5. Fluorescence images of a ODTMS monolayer in a pure water subphase of pH = 10.6. The images are taken at the points indicated in Figure 3. The scale bar corresponds to 100 μ m.

Fluorescence Microscopy. The clear LE–LC coexistence region in the compression isotherm of ODTMS at intermediate pH makes epifluorescence microscopy a suitable tool for the investigation of the phase equilibria in this system. Images taken at the points indicated in Figure 3 are shown in Figure 5. The LC domains form at π_{tr} and grow during compression, as seen from panels a–c. The ripening process showed up very clearly in the images, and normally pairs of small domains were formed prior to ripening. The phase equilibrium was described by a lever rule,¹⁶ and the domain growth was perfectly reversible at intermediate pH values. However, hysteresis in the compression isotherm was observed at pH values where the compression isotherms were intermediate between the condensed and expanded type isotherms. Since this behavior was thought to result from chemical and physical changes in the monolayer, epifluorescence micrographs were also taken at different times during the surface pressure relaxation experiments, in order to determine what kind of processes were responsible for the observed pH-dependent decrease in surface pressure. Immediately after spreading, a uniform bright image was observed, in agreement with the fact that the monolayer initially should remain in the LE state at this surface pressure. However, eventually dark spots appeared in the images, corresponding to the formation of a condensed phase in the monolayer. The domains appeared in the images at a surface pressure of about 6.5 mN/m and continued to grow with time as independent units throughout the region corresponding to fast relaxation in the surface pressure decay curves. When the surface pressure reached the plateau value, aggregation of the domains was observed. However, the shape and size of the domains was crucially dependent on the pH. This is clearly seen in Figures 6 and 7, where fluorescence micrographs obtained at pH = 4.1 and pH = 11.4, respectively, taken at the points indicated in Figure 2 are shown. These pH values fall in the time region of intermediate surface pressure relaxation and allowed us to follow the development of the aggregation process without the experimental difficulties arising from the following reasons: (i) At extreme pH the aggregation occurred within seconds, making it difficult to follow the early stages of the process. (ii) At intermediate pH values the aggregation process was so slow that surface contamination and water evaporation could have influenced the results. At pH = 4.1 the growth of the domains resulted in starlike structures, which implies that the growth occurs continuously in discrete directions. These

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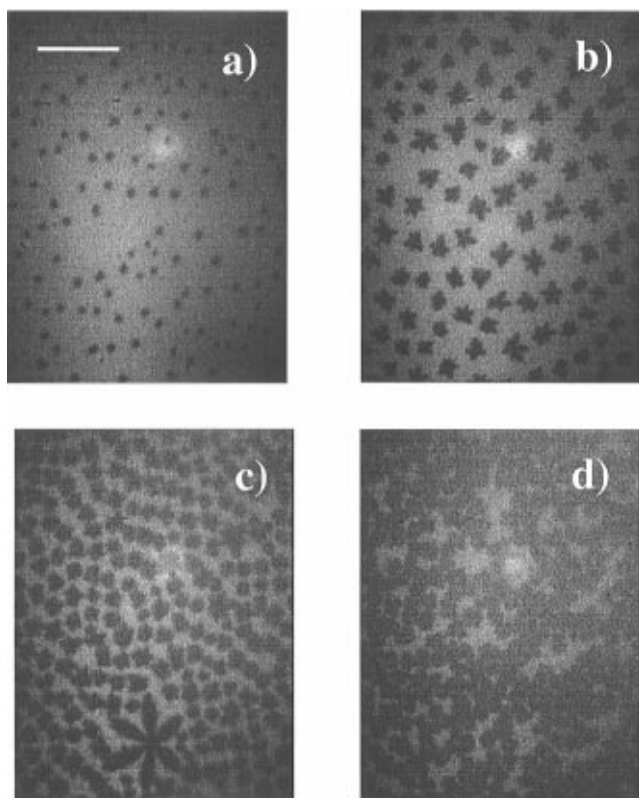


Figure 6. Fluorescence images obtained after different times of a ODTMS monolayer held at a constant mean molecular area of 0.50 nm^2 at $\text{pH} = 4.1$. The images are taken at the points indicated in Figure 2. The scale bar corresponds to $100 \mu\text{m}$.

structures might eventually grow considerably in size, and occasionally domains with a radius $> 100 \mu\text{m}$ were observed. When the plateau pressure was reached, two-dimensional gelation of the monolayer occurred, which finally resulted in a two-dimensional gel. The gel was very stiff and did not rearrange on blowing on the surface, indicating that a true gel had formed. The starlike structures observed at $\text{pH} = 4.1$ were also observed between $\text{pH} = 3$ and 7 . It should be noted that the shape of these domains was different from those observed in the LE-LC coexistence region at intermediate pH , which formed reversibly and where the domain size was governed by the lever rule. However, at lower pH , where the domain growth was faster, the star-shaped domains appeared also during the compression measurement. Furthermore, these domains formed irreversibly, since changing the monolayer area did not affect the size of these domains once formed. The solid nature of these domains suggests that the domains consist of condensed rather than hydrolyzed species.

At $\text{pH} < 4$, however, where the surface pressure decay was rapid, the domain sizes decreased and very dense gel type structures were formed without any sign of the large starlike aggregates occasionally observed at $\text{pH} 4\text{--}7$. Therefore it may be concluded that fast growth resulted in smaller, more uniform domains. At $\text{pH} = 11.4$ smaller circular domains were observed. However, the domains did aggregate into open, floc-like structures in the region where the plateau pressure had been reached. The aggregate structure did not correspond to a gel, since clear rearrangement of the aggregates occurred when air was gently blown upon the surface. If the pH was further increased, much more compact aggregates with a more or less continuous structure were formed within a couple of minutes after spreading. This was surprising, since the

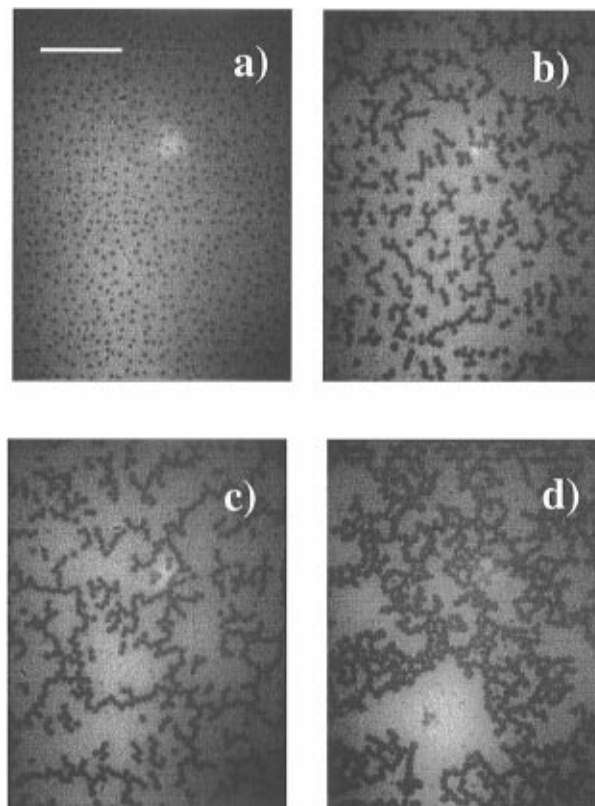
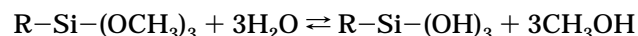


Figure 7. Fluorescence images obtained after different times of a ODTMS monolayer held at a constant mean molecular area of 0.50 nm^2 at $\text{pH} = 11.4$. The images are taken at the points indicated in Figure 2. The scale bar corresponds to $100 \mu\text{m}$.

monolayer should be negatively charged at these pH values. However, the ionic strength was probably high enough to screen the electrostatic repulsion between the head groups, and aggregation could occur. Furthermore, a greater solubility at extreme pH should result in the formation of much more compact structures.¹⁹ If the monolayers were compressed at a time when no changes in the gelation/aggregation structure were observed in the images, condensed monolayers with no sign of the LE state were seen.

Discussion

The hydrolysis of ODTMS may be written



However, this description of simple hydrolysis of the methoxy groups is an oversimplification. There are several reasons for this discrepancy: the hydrolysis rate of the remaining methoxy groups increases once a methoxy group has been hydrolyzed, the hydrolysis reaction induces changes in the effective pH at the interface, and direct condensation between hydrolyzed and unhydrolyzed species may also occur.^{15,17} Once hydrolyzed, the state of the monomeric silanol head group depends on the pH of the subphase. $\text{Si}(\text{OH})_4$ is a weak acid, with a reported pK_a value of 9.8 .^{18,19} $\text{C}_{18}\text{H}_{37}\text{-Si}-(\text{OH})_3$ should be an even weaker acid than $\text{Si}(\text{OH})_4$, since the C_{18} chain is expected to enhance the electron density around the polar group.⁹ Furthermore, there might be additional shifts in pK_a of several units arising from differences in the local environment between the interfacial region and the bulk, as

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observed for fatty acid monolayers. Firstly, the electric double-layer potential, ψ , built up at the interface as the siloxane groups dissociate will oppose further ionization by attracting hydrogen ions to the interface.²⁰ Secondly, there might be a nonelectrostatic contribution arising from a possible lowering of the dielectric constant at the interface.²¹ Both these effects will cause an increase in the effective pK_a . Therefore, it is not surprising that extensive dissociation of the ODTMS monolayer is not observed at $pH < 12$.

The ability to distinguish between the hydrolysis and condensation reactions in the monolayer is crucial for the interpretation of the results presented in this study. Ariga and Okahata⁸ performed FT-IR on multilayers of [γ -(octadecylsuccinyl)amino]propyl]triethoxysilane deposited on a CaF_2 plate at $pH = 2$ and $pH = 5.8$. At $pH = 5.8$ the Si–O–C stretching at 1080 and 1103 cm^{-1} was present in the spectra, suggesting that the monolayer existed in its monomeric, unhydrolyzed form at this pH. At $pH = 2$, however, the spectra showed clear absorption at 1026 and 1095 cm^{-1} , which was attributed to the Si–O–Si stretchings, suggesting that the monolayer was polymerized. Sjöblom and co-workers⁹ performed XPS measurements on multilayers of octadecyltrimethoxysilane deposited on glass substrates at $pH = 1$, $pH = 5.6$, and $pH = 11$, respectively. At $pH = 1$ the monolayer was completely polymerized, while only a very small fraction, 3–4%, of the monolayer was polymerized at $pH = 5.6$ and $pH = 11$. However, if the deposition process was started after a waiting period of 16 h, at the deposition pressure fully polymerized monolayers were observed. The hydrolysis of the silane head group is clearly responsible for the observed suppression of the LE state in the compression isotherms, due to the much smaller size of the hydrolyzed head group. However, the condensation reaction should not give rise to a change in the area occupied by an ODTMS molecule. It is evident from results presented in this study that the pH dependence of the hydrolysis/condensation of the ODTMS monolayer may be divided into four different regions, as indicated in Figure 4. On the basis of these observations and the spectroscopic data found in the literature, we interpret the results as follows: In region I the monolayer consists of hydrolyzed/condensed and slightly positively charged species. In region II a hydrolyzed/condensed monolayer has formed and the monolayer is at its point of zero charge, pzc. In region III the monolayer remains unhydrolyzed. In region IV the monolayer is hydrolyzed/condensed and slightly negatively charged, especially at $pH > 12$. It should be remembered, however, that the pH interval corresponding to unhydrolyzed ODTMS depends on the time allowed between spreading of the monolayer and initiation of the compression, the longer the time the narrower the interval will be, due to continuous hydrolysis in the monolayer. The increased degree of ionization at low- and high-pH values did not result in an expansion of the monolayer, as seen in Figure 1. However, the high ionic strength of the subphase in these pH regions should screen any electrostatic interaction between the surfactant head groups. The pzc of silica has been determined to be between 2 and 3,¹⁸ in good agreement with the value obtained for ODTMS in this study. This fact highlights the value of measuring the surface potential of spread monolayers. The observation that a pH of 12 was needed in the high-pH end to obtain the same condensation level as observed for a pH of 3 suggests that H^+ is more efficient than OH^- in catalyzing the hydrolysis of the methoxy

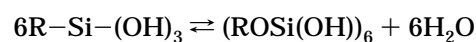
groups. However, as is evident from the fluorescence microscopy images, the mean molecular area obtained from the compression isotherms of fully condensed monolayers will not have any physical significance on the molecular scale but rather give information about the compressibility of the aggregates formed. The observation that the area where the surface pressure starts to rise at $pH = 11$ is dependent on the compression speed, i.e. higher areas were observed at higher compression speeds,⁹ may clearly be attributed to the ability of the surface flocs to rearrange at lower compression speeds and to the potential of further hydrolysis of the silane head group during the time of the compression experiment. No such dependence on the compression speed was observed at $pH = 5.6$, in agreement with our results that no gelation occurred within 10 h after spreading at this pH. Wood and Sharma²² reported that a monolayer of octadecyltriethoxysilane at $pH = 2$ required a waiting time of 30 min after spreading to obtain the most condensed monolayer structures while the data of Barton and co-workers¹⁰ suggest that a waiting time of less than 5 min was enough for monolayers of octadecyltrichlorosilane to undergo condensation at this pH.

A very plausible explanation for the LE–LC transition observed for unhydrolyzed ODTMS monolayers has been given by Taylor,²³ who suggested that the transition is induced by close packing of the polar head group. In other words, the monolayer may be thought to consist of two separate regions with individual packing properties: one being the hydrocarbon part of the monolayer and the other being the polar part. Upon further compression, undulation, or “collapse” of the polar part of the monolayer, occurs and the mean molecular area in the solid state is determined by the hydrocarbon part of the surfactant.

Kinetics of the Nucleation and Growth Process.

The shape of the surface pressure relaxation curves and the observed growth of the domains with time are clearly consistent with a nucleation and growth process. However, the initial nuclei are too small to be visible with epifluorescence microscopy, since the resolution of the fluorescence microscope was about 1 μm . The observation that H^+ and OH^- exhibit specific catalytic activity on the hydrolysis and condensation of methoxysilanes in bulk sol-gel processes holds true also for the corresponding reactions in two dimensions, since the rate of the nucleation and growth process seems to be directly correlated to the concentration of these ions in the subphase. A major difference between two- and three-dimensional systems is that condensation seems to occur immediately after hydrolysis in two-dimensional films, while the condensation reaction may require several hours or even days to finish after hydrolysis has occurred in three dimensions.

The sixfold symmetry of the domains observed at $pH = 4–7$ may indicate that the building blocks of the domains possess a hexagonal symmetry. A hexagonal symmetry may be achieved by the formation of ring structures, like uncharged hexamers, in the monolayer, which may be written as



Indeed, the formation of ring structures has been proposed to account for the early stages of polymerization of silica followed by addition of monomer or cyclic structures to produce larger three-dimensional aggregates in the sol-

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gel process.¹⁸ Star-shaped domains have also been observed in a recent study on the same material.¹⁵ In this study, the ODTMS monolayer was spread to 0.60 nm² at neutral pH and then the pH of the subphase was lowered to pH = 2 ± 0.5. In this study another fluorescent probe was used, indicating that the chemical properties of the probe did not influence the observed domain shapes. Concentrated solutions of SiO₂ and Na₂O or K₂O of ratio 1:1 to 1:2 consist mainly of SiO₃²⁻ and HSiO⁻ ions. It has been proposed that in solutions of higher SiO₂/M₂O ratio an increasing proportion of the silica will form small, three-dimensional, internally condensed silicate polymer ions or charged particles. These have been reported to generally be equiaxed or spherical in shape, each silicon atom on the exterior bearing at least one OH group.¹⁸ Even though the particles observed in the sol-gel process are extremely small, we suggest that our observation of round domains in the monolayer may be explained by the presence of charged, condensed aggregates. Generally the shape of the domains is ascribed to the interplay between two effects: (i) the line-tension, the two-dimensional equality to the surface tension, which is responsible for the formation of circular domains, and (ii) the electrostatic repulsion between similarly charged head groups, leading to fractal domains.²⁴ In our study the opposite was observed; circular domains were observed at pH values where the head groups were charged, and starlike domains were observed at pH values where the

monolayer was uncharged. This observation suggests that the shape of the domains might change dramatically if the aggregation involves formation of chemical bonds between the head groups. Furthermore, the high ionic strength at high pH screens the electrostatic repulsion between the head groups, preventing the formation of fractal domains. The results may also indicate that intermediate ring structures were not formed at high pH.

Summary

ODTMS forms insoluble monolayers in the pH region 0.5–13.5. Fully condensed monolayers were observed at pH < 3.5 and pH > 12.5, respectively, indicating that the methoxy groups were hydrolyzed. The fluorescence microscopy images suggested that the subsequent condensation of the hydrolyzed methoxy groups occurred immediately after hydrolysis. The dissociation of the hydrolyzed monolayer could be followed by surface potential measurements, while the compression isotherms were insensitive toward the presence of charges in the polar region. This feature was explained by the high salinity of the subphase at extreme pH, screening the electrostatic repulsion between like charges.

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