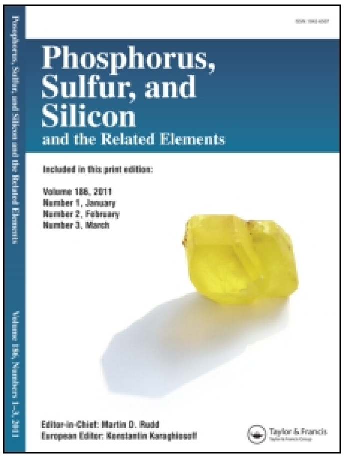

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PLENARY AND INVITED LECTURES

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Formation, Behaviour and Reactivity in Thin Organic Films Containing Sulfur

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The theme of this lecture is concerned with the change in behaviour of simple molecules which occurs when such molecules are incorporated into assembled or self-assembled mono- and multilayers on surfaces. The area is one of wide technological importance because of potential application in, for examples, photoresists, piezo and pyroelectric devices, and multiple harmonic oscillators[1]. Behaviour of assembled molecules is also significant because of the nature of lipid bilayer cell membranes and their behaviour is, of course, of front-line importance in connection with matters such as inherent stability and penetration by drugs and so on. This account is concentrated upon events at the molecular level and the emphasis is on the relationship between structure and selectivity.

Historical Introduction

The behaviour of thin films was familiar in antiquity and experience usually related to thin films of insoluble materials on the surface of water. To pour oil on troubled waters is a familiar expression and an early example is the throwing of Jonah overboard in order to mitigate the effects of a Mediterranean storm.[2] The first quantitative experiment was conducted by Benjamin Franklin[3] in 1774 when he put a small spoonful of fish oil over the side of a boat on a pond in Clapham Common in South London and was surprised to see the film of oil spread to the boundaries of the pond. He was able to measure the thickness of the layer which corresponded well with thicknesses of monolayers obtained by modern methods. More than 100 years later Agnes Pockels, a young Austrian woman, keenly interested in experimental science, was prevented by her father from going to University and the frustrated experimenter carried out the first experiments on the surface pressures of thin films, literally on saucepans in her kitchen. The surface detector was a shirt button hanging on a thread. This simple but elegant experimentation came to the notice of Lord Rayleigh in London who helped her to develop her career in science.

Much the best known pioneer of surface chemistry was Irving Langmuir, the first person from an industrial laboratory to be awarded the Nobel Prize in chemistry. Langmuir's contribution to surface chemistry was very wide ranging but he is, of course, best known for the design of the Langmuir trough using barriers essentially designed by Agnes Pockels and with accurate surface pressure determinations using a Wilhelmy plate. (Figure 1). The information that can be obtained about such surface films with a Langmuir trough are the π-A curves which show surface pressure versus the area of the material laid down which can, of course, be directly related to the area per molecule. Information is readily obtained about the stability of films, their collapse pressures and the progress of molecular ordering as surface pressure on the film is increased. A typical plot is in Figure 2 where it can be seen that at low pressures the molecules behave as essentially random individuals with their hydrophilic tips in the water surface and under these conditions can be likened to a two-dimensional gas. As the surface pressure is increased the molecules are forced closer together and the compressibility of the system decreases. Under these conditions there is often a phase transition as shown in the figure and when the compressibility becomes low the molecules can be likened to those of a poorly compressible liquid. Under further compression there is further small contraction of the area and in this part of the curve the surface molecules behave as a two dimensional solid. Further pressure causes film collapse, usually to give a bilayer.

Figure 1. Langmuir Trough

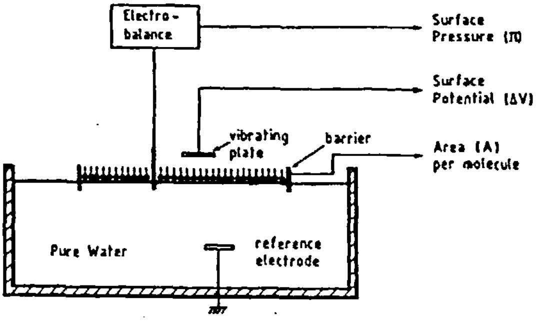
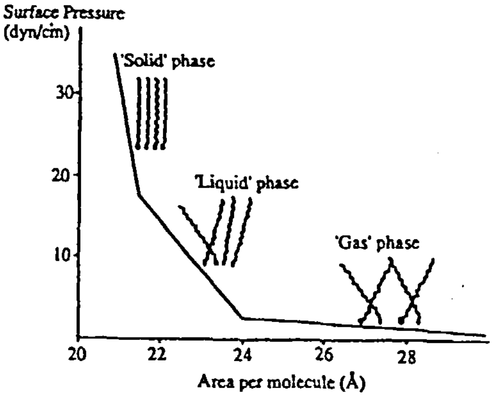


Figure 2. Schematic π/A curve for Stearic acid on 0.01M HCl.



The next important advance was made by Katharine Blodgett working in Langmuir's laboratory who attacked the problem of removing monolayers onto solid substrates for more convenient examination. The secret is to use a thin sheet of solid (the substrate) often a microscope slide or a sheet of silicon, which is dipped to and fro through the surface of the film keeping the surface pressure constant and hence preventing disruption of the film. In this way mono and multi layers of the material on the surface of the water can be built up (a typical example is shown in Figure 3) showing the deposition of some seven layers of a trifunctional carboxylic acid (1). As will be seen later, the Langmuir Blodgett technique is particularly useful for calibration of thicknesses of films deposited by other techniques.

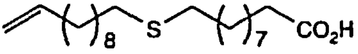


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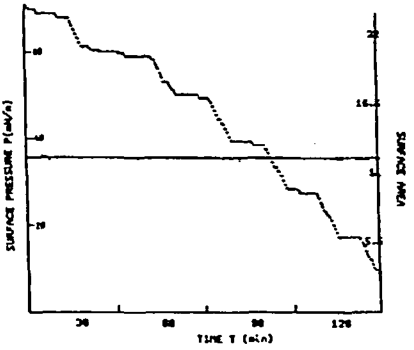
Figure 3. *Blodgett deposition of acid 1 in 6 layers.*



Formation of Thin Films

Two other very important techniques for forming assembled monolayers are, first, the Sagiv technique in which long chain silyl compounds are used to react with the surfaces of glass or quartz making covalent bonds thereby and giving extremely stable layers.[4] An even simpler technique is the gold-thiol monolayer procedure from which the results presented in this account are largely drawn. In this procedure, a gold coated substrate is dipped in dilute solutions of thiols forming strong gold sulphur bonds and highly ordered films which are mobile within the surface of the substrate. These gold-thiol monolayers are extremely versatile because deposition is not sensitive to the presence of other functional groups and provided that metal evaporators are available, no special equipment is required.[5]

Monitoring events at the surface of thin films

The amounts of material present in monolayers of organic compounds are very small typically of the order of 5 ng cm^{-2}. Consequently many conventional techniques for the routine monitoring of chemical events are not applicable. It is appropriate to review very briefly techniques available and their applicability in the work that follows. For further details the excellent text by Ulman[6] should be consulted.

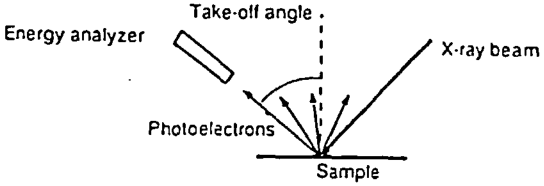
Surface microscopies

Two important techniques under this heading are surface tunnelling microscopy (see Figure 9b below) and atomic force microscopy. Both techniques have atomic resolution and enable the surfaces of, for example, gold thiol monolayers to be visualised. The main information that is available is the disposition of atoms and changes in the topology of surfaces. This is particularly important in dealing with defects in the surfaces of thin films of which little account can be taken by chemical methods.

X-ray photoelectron spectroscopy and neutron reflectometry

Again these techniques are appropriate for diagnosis of atom dispositions. X-ray photoelectron spectroscopy (XPS) is particularly useful for the placing and quantification of heavy atoms in layers and neutron reflectometry provides information on layer spacings which are important in considerations of multilayers. Signal strengths as a function of angle of incidence can also indicate positions of atoms in layers (Figure 4).

Figure 4. Schematic diagram of photoelectron spectroscopy



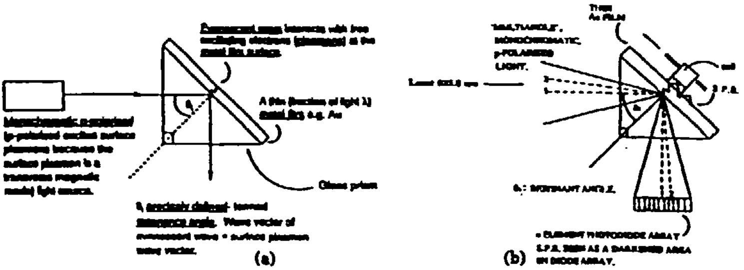
Quartz crystal microbalance

This is the first of two techniques which give us direct information on amounts of material in a monolayer and becomes important when adsorption into monolayers is considered. This technique is simple in principle but more complex in practice. A piezoelectric quartz crystal is excited to vibrate by the application of a potential and the vibrational frequency, typically in the region of 8 kHz, can be measured with an accuracy of 1 Hz. The vibrational frequency is lowered when materials are deposited on the crystal and with appropriate calibration, eg, by Langmuir Blodgett deposition, the device becomes a weighing machine with sub-nanogram sensitivity.

Surface plasmon resonance [7,8]

This technique detects changes in the amount of material at surfaces and also in their refractive index. It is, in principle, a simple optical technique in which a polarised light-beam is reflected from a metal mirror and in the process loses part of its energy to an evanescent wave which passes through the metal of the mirror and interacts with a monolayer or multilayer deposited on the other surface. Interaction with this monolayer is detected by a change in the resonant angle of the incident beam, ie, the angle at which there is the maximum reduction in intensity of the incident light beam. The device can be made very sophisticated as in the Pharmacia Biacore instrument or very simple as in our own homemade instrument (Figure 5a and 5b). While the device gives no direct structural information it is sensitive to about one fifth of a monolayer and is sensitive to refractive index change independently of mass change at the surface.

Figure 5a and 5b. Surface plasmon resonance (a) principle (b) practice

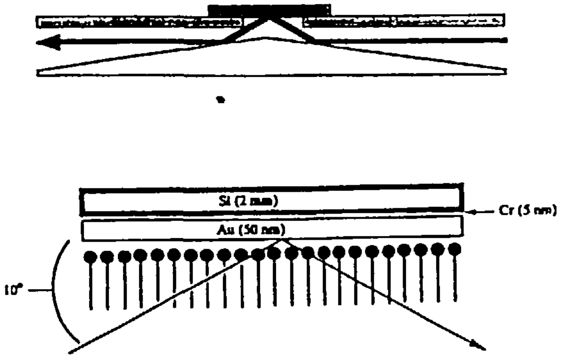


Polarised grazing angle reflection - adsorption FTIR spectroscopy

This is a modification of simple FTIR spectroscopy which is concentrated on increasing sensitivity because of the small amounts of material available. The main modifications are to use polarisation and a grazing angle of incidence which increases intensity of absorption (Figure

6). The FT mode allows multiple spectral superimposition and the use of an MCT detector increases sensitivity by a factor of about 10.

Figure 6. Polarized grazing angle FTIR spectroscopy



Ar Purge, 800 spectra in about 7 mins

Contact angle measurements

This is a superficially simple technique which involves measuring the contact angle between the thin film and a suitable liquid which is usually water but can also be, for example, hexadecane. The angle between the two materials is determined by their interaction and this is very sensitive to the nature of the surface (Figure 7). The difference between a hydrophilic surface and a hydrophobic surface can be readily detected by the naked eye. It is particularly useful for determining disorder in layer surfaces and for checking on build up of amphiphilic substrates as to whether a hydrophilic or a hydrophobic function is in the surface.

Figure 7. Contact angles of gold-thiol monolayer surfaces

Thiol	$\theta(H_2O)$	θ (Octadecane)
$HS(CH_2)_2CF_2CF_3$	118	71
$HS(CH_2)_{17}CH_3$	112	47
$HS(CH_2)_{19}Cl$	83	<5
$HS(CH_2)_{16}OCH_3$	75	41
$HS(CH_2)_{10}CONH_2$	13	<5
$HS(CH_2)_{15}CO_2H$	<10	<5
$HS(CH_2)_{11}OH$	<10	<5

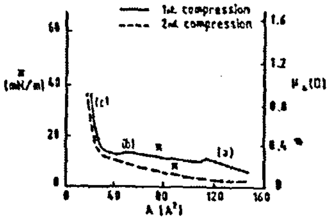
Domain Effects in Ordered Monolayers

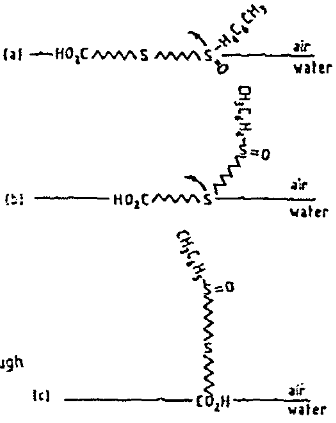
In any consideration of the nature of ordered monolayers, the question of arrangement at the substrate surface soon arises and inferences as to the situation may be drawn by a variety of techniques. In well-behaved situations, AFM and FTM can give direct information but do not give any hint of dynamic behaviour. Some information on the latter can be obtained in simple experiments which quickly indicate that monolayers are not simple infinitely cohesive structures. In Figure 8, the πA curve of the sulfoxide sulfide acid, **2**, is shown.

2

The pressure/area dependence is consistent with the molecules lying down on the surface at low compression, anchored by polar groups at both head and tail. As pressure increases the sulfoxide group is forced out of the water surface and under strong pressure the molecule stands up with its polar tail group in the air and with the cross-sectional area consistent with that of a simple carboxylic acid. In simple systems such as, for example, Langmuir films of steric acid there is generally no hysteresis and so when the pressure is relaxed the pressure area curve returns along the same pathway in the decompression as in the compression cycles. In Figure 8 it can be seen that there is considerable hysteresis between the first compression and the decompression because all future compressions follow curve b indicating that even at low compression there is a "memory" component in the film at low pressures. This may be due to clustering of the surface molecules into domains. This is a familiar phenomenon in bulk processes such as saw mill ponds in Canada where the logs become linearly oriented in areas of the pond and are not randomly scattered as, for example, in polar pack ice. Closer to the molecular level small spheres of polystyrene collect together on liquid surfaces[9a] (Figure 9a) and there are clear boundaries between one area and another. Domain boundaries in gold-thiol monolayers can be directly observed by STM[9b] (Figure 9b).

Figure 8. π-A curve for acid 2





- Differences between first and second compression-expansion cycles.
- Permanent molecular association through tail group interaction
- Ferro electric domains ? ?

Figure 9a. Domain behaviour in microsphere assemblies.

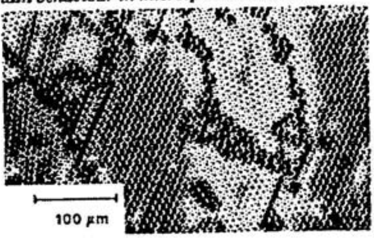


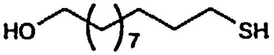
Figure 9b. Surface Tunnelling Microscopy image of a self-assembled monolayer (Molecular resolution)

The existence of such domain boundaries raises questions about the effect of such boundaries on the interpretation of the reactivity of films. In general boundaries are small by comparison with the ordered masses but, nevertheless, such defects in films may be the site of certain types of reaction.

We have obtained direct evidence of domain behaviour in a series of very simple experiments which arose from the question as to whether gold-thiol monolayers are mobile or fixed. Such films are probably mobile and we have made some simple observations. When a gold film is partially immersed in a dilute solution (Figure 10) of a thiol, eg, octadecanethiol, 3, it can be shown first of all that there is no

3

migration in the absence of solvent to the upper non-dipped part of the plate. The half dipped part of the plate shows the typical behaviour of hydrophobic layer with a high contact angle and, of course, infrared C-H adsorptions. The upper part of the plate shows the typical rather hydrophilic contact angle of pure gold. When the plate is now immersed entirely in solvent ethanol then the contact angle of previously empty area increases and that of the previously occupied area does not change. Infrared C-H adsorption appears in the upper half of the plate and the simple conclusion that can be drawn is that octodecanethiol molecules have migrated across the boundary. The question of occupancy in the newly occupied area arises. When this area is now dipped in a dilute solution of hydroxy-terminated long chain thiol, 4, the contact angle



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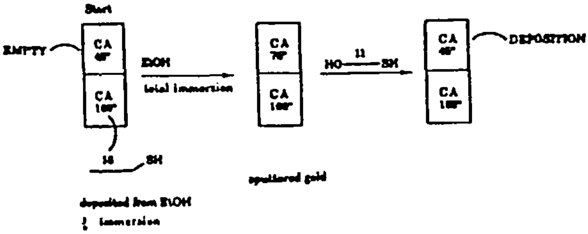
decreases again. This is consistent with deposition of a highly hydrophilic material. It looks, therefore, as though migration of octadecanethiol across the boundary does not prevent further deposition of individual molecules (Figure 10a).

Figure 10a. Gold-thiol molayer migration and deposition



Exactly the same type of behaviour can be observed when a long chain ester bearing a distal thiol group, 5, is deposited on half of a plate. When the plate is totally immersed, the carbonyl group of the ester can be seen on both sides of the boundary. When, however, octadecanethiol is deposited on one half of the plate and the long chain ester-thiol, 5, on the other half there is no migration of the ester across the boundary. This is shown by the failure of any carbonyl absorption to appear in that part of the slide which was inhabited by octadecanethiol. The simplest view of this experiment is that deposition of thiols on gold occurs in domains and that migration of these molecules occurs only collectively in the domain structure. This is consistent with the deposition of individual molecules in an area which is occupied by domains because space remains between the domains for such deposition. On the other hand, when deposition is entirely in the form of domains in both halves of a coated plate but with different molecules in the domains then there is not sufficient space for domains to migrate on any short time scale, and mixing does not occur (Figure 10b).

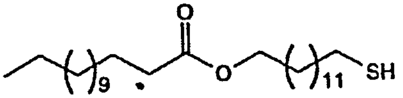


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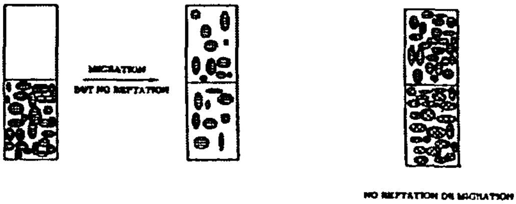
Figure 10b. Domain migration and non-migration



Self-assembly of several branched thiols possessing two long alkane chains and corresponding disulfides on gold surfaces has been investigated [10] by contact angle measurements, Fourier transform infrared spectroscopy (FT-IR), surface plasmon resonance (SPR), and atomic force microscopy (AFM). Monolayers formed by the disulfides were shown to be significantly thinner (SPR) and much more disordered (FT-IR, contact angles) than SAMs of the thiol counterparts. The presence of polar functional groups and complementary H-bond donors/acceptors in the alkane chains of branched disulfides was shown to assist the formation of better packed monolayers. Compared to SAMs of octadecanethiol, the branched thiols investigated in this study gave SAMs with a significantly reduced tilt angle, as seen in the FT-IR spectra. AFM revealed the lattice of one of the thiols on Au(111) with molecular (lattice) resolution showing a reduced area per molecule (as compared to octadecanethiol) which is consistent with a reduced tilt angle.

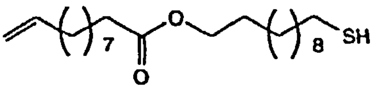
Reactions and Adsorption Phenomena in Monolayers

Ester Hydrolysis

Infrared spectroscopy coupled with contact angle information as confirmatory back up gives direct information on functional group changes even at the monolayer level. The ability to make such observations allows general questions about the reactivity of functional groups in the surface and below the surface of monolayers to be asked. The simple long chain ester thiol 6 can be deposited in the usual way and when the

6

functionalised surfaces are exposed to methanolic solutions of sodium methoxide, transesterification occurs with loss of the carbonyl group in the film. The rate of reaction is somewhat dependent upon the precise nature of the preparation of the gold surface, varying particularly as to whether it is done by sputtering (which produces less well ordered surfaces and hence less well ordered films) and plasma deposition which produces very regular surfaces. It is necessary, therefore, to compare like with like in this area and when reactivity of ester 5 in a monolayer towards transesterification is compared with that of ester 7 in which the ester function is buried well



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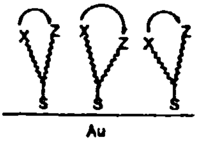
below the surface in the ordered monolayer then, unsurprisingly, there is a very large difference in reactivity. Reaction with the buried functional group cannot be observed. When sputtered gold is used the surface ester is at least 10 times more reactive than the buried ester (this is probably an underestimate by two or three powers of 10!). The check experiment in which the reactivity of the esters is compared in bulk solution was, of course, carried out. The reactivities are the same. When enzymic hydrolysis using pig liver esterase was applied to these functionalised surfaces, then again very substantial differences in reactivity of the plasma gold specimens was observed. There was slow removal of the carbonyl group in the case of the surface ester and the buried ester did not react at all over a considerable period. A striking observation, however, was that in the carbonyl region of the infrared spectra, strong amide I and II bands appeared and increased in intensity steadily throughout the experiment[11]This apparent deposition of protein is also occurs with a layer of octadecanethiol and so the hydrophilicity of the surface is clearly not a factor in such deposition. This phenomenon is a generally important one in relation to such superficially mundane matters as the pumping of biological materials .

In very recent work,[12] sigmoid kinetic behavior was found by FTIR spectroscopy in the alkaline hydrolysis of ester groups in well-packed self-assembled monolayers (SAMS) of thiols and the corresponding symmetric disulfides. Asymmetric disulfides terminated by ester and by hydroxyl groups, however, exhibit fast (pseudofirst order) exponential kinetics in similar hydrolyses. The same reaction were investigated *in situ* on a scale of less than 100 molecules in atomic force microscopy (AFM) experiments using tips modified with these SAMs and measuring the pulloff forces on an inert SAM substrate. The observed induction periods for the thiol and the symmetric disulfide are attributed to restricted access of the external reagent to the carbonyl group buried under the surface of the monolayer. Our studies reveal that the surface reaction spreads outwards from defect sites, leading to separation of the originally homogeneous SAMs of the thiol and symmetric disulfide into domains of reacted and unreacted molecules. At the surface of the films of the mixed disulfide, the attack of the hydroxide ions is, however, random.

Recently, we have examined[13] reactivity in the intra- and intermolecular aminolysis of esters in monolayers *versus* bulk media. Monolayers possessing reactive amino and *p*-nitrophenyl ester functional groups at the same or different levels with respect to the monolayer interface have been self-assembled on a gold surface (Figure 11 and Chart 1) Intramolecular reactions in these monolayers are at least 1000 times slower than the same processes in the bulk medium (Scheme 1) Control experiments with external reagents showed that the monolayer *p*-nitrophenyl ester group reacts readily with amines from solution, whereas nucleophilicity of the monolayer amino functionality is significantly suppressed. This unusually low reactivity of the amino group was tentatively assigned to its interaction with the gold surface.

Figure 11



Schematic illustration of a bifunctional monolayer with two reactive functional groups (X and Z) incorpora therein.

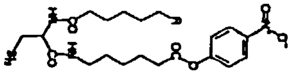
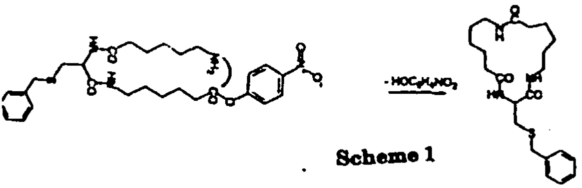
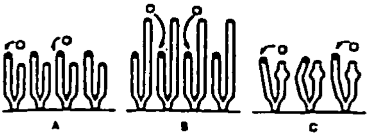


Chart 1

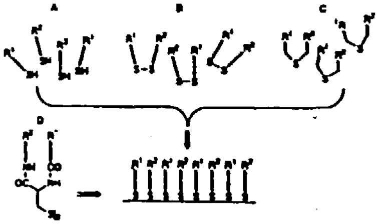


Scheme 1

Monolayers containing a reactive *p*–nitrophenyl ester group at different levels with respect to the monolayer interface have been self-assembled on a gold surface (Chart 2). Analysis of grazing angle IR spectra, surface plasmon resonance (SPR), and wettability measurements suggests disordered organization of the alkane chains in the monolayers. Kinetics of monolayer reactions with external reagents(alkylamines) have been studied and compared with those of the same process in bulk medium.[14] Burying of a reaction center under the surface and other structural changes of monolavers were shown to have only a minor effect on the rates of reaction, implying that these monolayers could be easily penetrated by guest molecules. The higher reaction rates with monolayers than in bulk solution are possibly due to a weak binding of the external reagent to the monolayer prior to reaction.

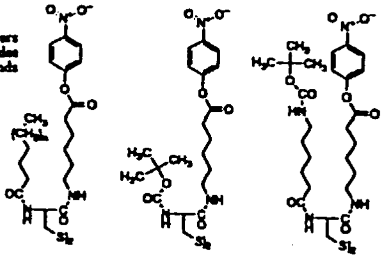


Schematic illustration of different positions of the reactive functional group (shown as black circles) in a monolayer: protruding above the interface (A), buried inside the monolayer (B), and incorporated into a disordered monolayer (C). Approach of an external reagent (shown as open circles) to the functional group is shown with arrows.



Schematic formation of bifunctional monolayers using a mixture of different thiols (A), unsymmetrical disulfides (B), dialkyl sulfides (C), and cystine-based Y-type compounds (D).

Chart 2



Adsorption by an enantiopure surface

The use of a chiral functional group at the distal end from the thiol anchoring group in an appropriate thin layer-forming molecule has the potential for the formation of enantiopure surfaces. Surprisingly this is a very little investigated area[15],and we have only made preliminary experiments [16] which we shall develop. We chose the sulfoxide-thiol 8

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readily obtained enantiopure by the Andersen synthesis and monolayers on gold were readily formed. The question about such surfaces was whether they would be selective in the adsorption of one enantiomer rather than the other from a racemic mixture and what the degree of selectivity would be. We required an adsorbate which was readily available in both enantiomeric forms, was volatile, possessed a hydrogen bonding functional group and an infrared active functional group so that we could observe adsorption. Against these criteria we chose ethyl lactate, **9**. In initial experiments, monolayers of the sulfoxide were exposed to the

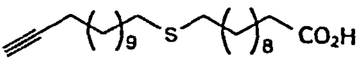
$$CH_3CHOHCO_2Et$$

9

vapour of racemic ethyl lactate, typical conditions being 16 hours at 20°. Any surplus ester that may have condensed on the plates was removed *in vacuo* under standard conditions. The plates were then washed with dichloromethane, the washings concentrated and the concentrate examined by chromatography on a cyclodextrin B column which had been shown to be capable of base line separation of the enantiomers. With short exposure at ambient temperatures, adsorption of the ester readily discernible by infrared spectroscopy was completely non-selective with ratios of 1.1 ± 0.02. This result suggests stereochemically either that there is no selection, which under the circumstances seems improbable, or that there was indeed selection to form a new homochiral surface. This surface would then be expected to be more receptive to the opposite enantiomer than to the same enantiomer against the background of the fact that the known free energies of racemic mixtures are lower than those of the pure enantiomers. On the nanogram scale this was a difficult matter to be sure about and we felt that a more likely explanation was that the surfaces were not in fact in equilibrium with the enantiomer mixtures. When the experiments were repeated at higher temperatures and for longer exposure times the surfaces ultimately became completely stereoselective, only one enantiomer being detected in the wash-off solvents. The absolute configuration of the sulfoxide is known from the Andersen synthesis as is, of course, the absolute configuration of ethyl lactate. Models are consistent with the observed stereoselectivity.

Polymerisation of adsorbates

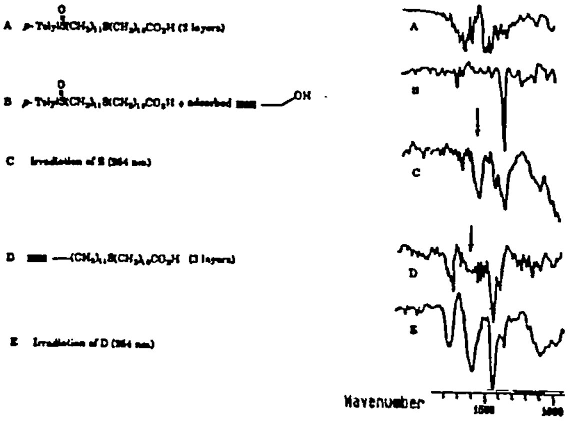
An obvious general question to raise in terms of the behaviour of molecules in monolayers is whether their behaviour is any different from that shown in bulk solution. There is already considerable anecdotal evidence about the different behaviour of molecules covalently bound in monolayers. For example, the formation of monolayers of bisacetylenes and their subsequent polymerisation by irradiation has been well described. Such systems are set up for polymerisation by the enforced juxtaposition of the polymerisable function. We wondered whether it would be possible to adsorb on a functionalised surface a molecule which would not of itself be susceptible to polymerisation under irradiation. We chose the surface previously formed from sulfoxide **2** and allowed the vapour of but-3-yn-1-ol to adsorb on it. The surface was then irradiated with uv at 254 nm and the resulting spectral changes are shown in Figure 12. The striking difference in the spectra before and after irradiation is in the absorption at 1600 cm-1 consistent with the formation of a conjugated polyene[17] The corresponding check experiment (check experiments pervade this area of chemistry) is to examine the spectral changes contingent upon irradiation of the alkyne terminated carboxylic acid **10**. Whên Langmuir Blodgett



10

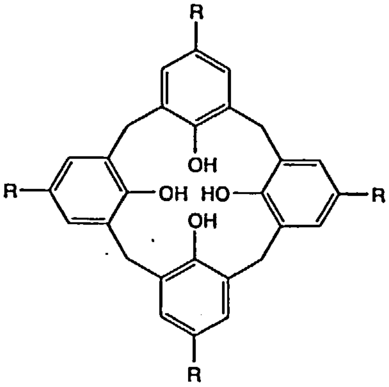
films of this acid were irradiated, (Figure 12) an intense band at 1600 cm^{-1}developed as for the adsorbed butynol spectrum. It appears, therefore, that order in a film imparts order to an adsorbate and it is this order which imparts new properties to the adsorbate. This is, presumably, because of enforced juxtaposition of the adsorbed molecules and this is, of course, a general theme in this area of thin film chemistry. Further examples appear below.

Figure 12. FTIR observation of polymerisation of surface-adsorbed but-3-yn-1-ol



Host-guest chemistry in thin organic films - selective adsorption by calixresorcinarenes

Calixarenes as a class of organic compound have been known for more than 50 years[18] but their chemistry has had great stimulation with the advent of supramolecular concepts in chemistry and the specific investigation of selective adsorption of both inorganic and organic species by members of this large class of molecules. Our particular interest in this type of molecule was focused on the possibility of innobilising them in a regular way as gold-thiol monolayers on the one hand and of using them as potential reptands on the other. Their synthesis is remarkably simple; treatment of an appropriate aldehyde with an appropriate substituted phenol gives a simple calixarene **11** and when a similar reaction is carried out with resorcinol instead of a simple phenol then the result is a calixresorcinarene **12**.



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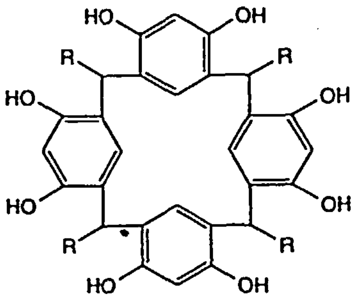
out with resorcinol instead of a simple phenol then the result is a calixresorcinarene **12**. These molecules are available cheaply and in high



12

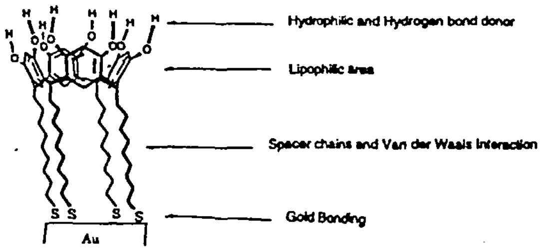
yield by the simplest of procedures and the result, for example, of reacting resorcinol with undecanal is calixarene **13** obtained in 87% yield and with

$$R = -(CH_2)_{10}CH_3$$

13

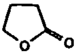
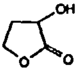
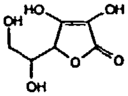
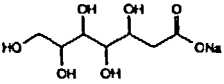
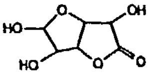
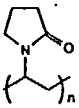
Van der Waals interactions. We have placed thiol groups at the end of each of the four legs by appropriate simple synthetic procedures and the thiol-footed resorcarene **14** readily forms a gold thiol monolayer in which, as shown by contact angle measurements, the bowls are at the surface (Figure 13.)

Figure 13. *Calixresorcinarene* **14** *in a gold-thiol monolayer*



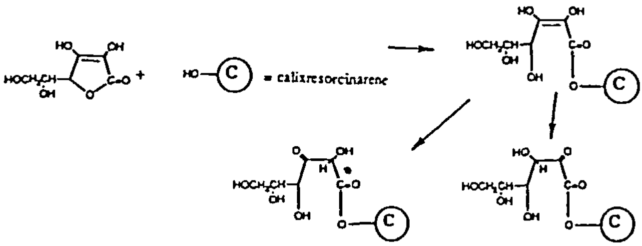
Aoyama and his collaborators[19] had shown earlier that a variety of polyhydroxy compounds readily complexed with calixarenes in bulk conditions. With this in mind we examined the series of potential adsorbates in Table 1[20] together with an extensive series of related ones.[21] In all cases we chose substrates that were infrared active so that we could monitor both adsorption and desorption.

Table 1. Substrate binding by a calix-4-resorcinarene monolayer 14.

Substrate	Adsorbed	Washout	Substrate	Adsorbed	Washout
	Yes	Yes	$\bar{N}_3$	No	
	Yes	No		Yes	Yes
	Yes	No		Yes	Yes
	Yes	No		Yes	Yes

The adsorbates fell into three categories. First, those which were not adsorbed such as azide ion. Second, those which were readily adsorbed and readily desorbed. Into this class fell simple carboxylic acids such as glutaric acid and salts of hydroxy acids such as sodium gluconate. The third category, however, comprised hydroxy-lactones such as Vitamin C, glucurono-6,3-lactone and α-hydroxy-γ butyrolactone. The behaviour of these compounds was striking in that not only was there a considerable difference between the bulk and adsorbed spectra of the adsorbate but when films with these adsorbed substrates were treated with dilute aqueous sodium hydroxide, the adsorbate was released. We tentatively attribute this behaviour to acylation of the hydroxyl groups on the periphery of the bowl by the lactone ring of these adsorbates. One could imagine that this is a case of nucleophilic catalysis (bowl hydroxy-nucleophile) and general acid catalysis (bowl hydroxyl acid) of the formation of the tetrahedral intermediate. Release of the trapped ester in the presence of aqueous sodium hydroxide is then understandable. We are not yet certain of the generality of such a process (Scheme 2). Simple non-cyclic hydroxy esters, half ester half acid and acylated calixarenes are all obvious check systems.

Scheme 2 **Lactone - Calixresorcinarene Reactions?**



We have used thiol anchoring groups; significant prior work by Reinhoudt and his collaborators[22] at Twente demonstrated the use of sulfide anchoring groups in these molecules. The existence of these long chains coupled to the hydrophilic bowls suggested the possibility of bilayering in such molecules. We showed that when an immobilised layer of calixarene **14** as a gold-thiol monolayer was treated with a dilute solution of the simple calixresorcinarene **13** with no thiol groups, the contact angle confirmed that the surface of the new layer was now hydrophobic. This is in contrast to the hydrophilic nature of the simple bowl-up monolayer. Infrared spectra, however, showed that to judge by the intensity of the C-H stretching absorption in the infrared spectrum, not a bilayer but some 40 layers had been deposited. This deposition was found to be slightly dependent on the concentration of the simple calixarene in solution and, very importantly, the deposition occurred from non-polar solvents such as hexane and not at all from, for example, ethanol. When the hydrophobic layers produced in this way were treated with a polar solvent, then the hydrophilicity of the layer returned to that of the simple monolayer. These multi-layers were resistant to ultrasonication in hexane and we are confident that this is not a random deposition onto the surface. We believe that there is a bowl to bowl hydrogen bonded interaction and a tail to tail Van der Waals interaction with deep interdigitation of the tails. This view is entirely supported by the single crystal X-ray structure of calixarene **13** (Figure 14) which shows interdigitation of the legs to within one atom of the opposing bowl. In interpreting the structure of the apparent multilayers, the thickness of these, of course, is crucial and these have been determined by neutron reflectometry[23] giving dimensions in the layer which are entirely consistent with the number of layers indicated by the enhancement of the intensity of the C-H stretching vibration. We are confident, therefore, about the nature of these multilayers[24] with the single reservation that the top surface may, in fact, be rather disordered (Figure 15). This top surface fails to undergo reptation with long chain ester, azide or sulfonic ester and we cannot at present interpret this observation on any other basis.

Figure 14. X-ray crystal structure of calixresorcinarene **13**

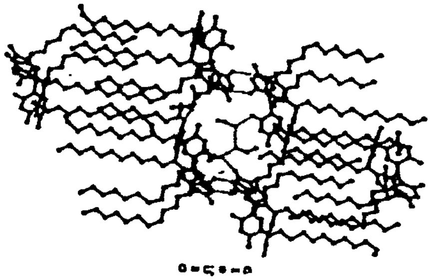
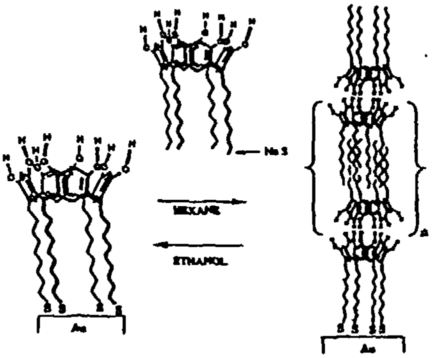


Figure 15. Multilayering in calixresorcinarenes



Large change in Contact Angle (from 30° to 90°)

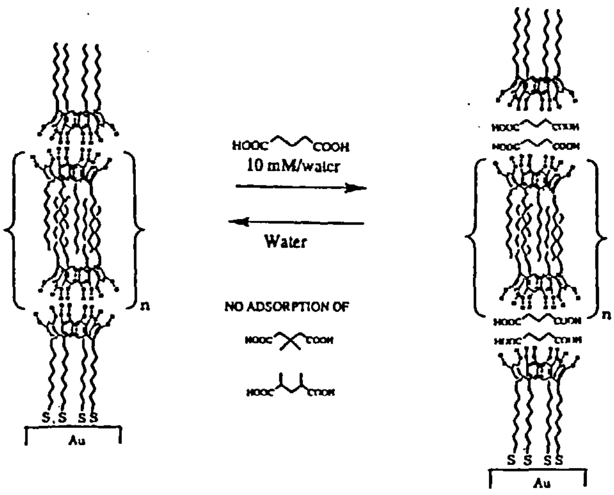
20 fold change in $\upsilon_{C\text{-}H}$ str intensity.

No inclusion of Vitamin C or
glucuronolactone
from aqueous solution
after 14 days.

No reptation of long chain substrates, eg. dodecyl azide, occurs.

These multilayering observations prompted another series of experiments. First, it was found that the multilayers formed by deposition of **13** on a gold thiol monolayer of calixarene **14** did not incorporate Vitamin C from aqueous solution,When, on the other hand, the Vitamin C adduct of the gold-thiol monolayer of **14** was then exposed to a hexane solution of calixarene **13**, a multilayer formed in the normal way showing enhanced C-H intensity and with the carbonyl group signal of the Vitamin C retained by the layer. When this layer, with Vitamin C incorporated, was washed with a polar solvent such as ethanol the multilayer was again removed leaving only the calixarene - Vitamin C adduct fastened to the gold below. In contrast, glutaric acid which is readily adsorbed and readily desorbed from the calixresorcinarene gold-thiol monolayer (Table 1), adsorbs readily from an aqueous solution into the multilayer. The stoichiometry, judging by the carbonyl and C-H stretching frequencies, is approximately 1 of acid to 1 of calixresorcinarene. When this glutaric-incorporated multilayer is then soaked in pure water, the glutaric acid is desorbed and carbonyl adsorption disappears from the infrared spectrum of the multilayer. Adsorption by the multilayer is clearly selective and it is selective to modification of the glutaric acid structure. When the 2,4-dimethyl or 3,3-dimethyl glutaric acids in aqueous solution are brought into contact with the gold-thiol monolayer or multilayers, no adsorption occurs (Figure 16). Clearly this adsorption is specific but the boundaries of specificity clearly need to be defined. This is an important trend in our current work.

Figure 16 Selective adsorption and desorption of glutaric acids



Acknowledgements

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