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Organized Monolayers by Adsorption. 1. Formation and Structure of Oleophobic Mixed Monolayers on Solid Surfaces

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Abstract: The possibility of producing oleophobic monolayers containing more than one component (mixed monolayers) is investigated. It is shown that homogeneous mixed monolayers containing components which are very different in their properties and molecular shape may be easily formed on various solid polar substrates by adsorption from organic solutions. Irreversible adsorption may also be achieved through covalent bonding of active silane molecules to the surface of the substrate. Details regarding the structure and the formation of mixed monolayers are revealed by means of spectroscopic methods using surface-active dyes as monolayer components. By studying the time dependence of formation it is shown that interactions involving both the molecules in the adsorbed state and those in solution lead to large fluctuations in the composition of mixed monolayers containing only reversibly adsorbed components, while irreversible adsorption tends to stabilize certain final compositions which are monotonically approached. It is concluded that adsorption on well-defined solid surfaces might be developed into a suitable method for producing monomolecular films with a controllable molecular organization.

I. Introduction

Much of the interest in organic monolayers stems from their relationship to biological membranes. However, their potential use as building elements of artificial systems with completely new properties is by no means less attractive. Kuhn and coworkers have demonstrated that planned structures showing order-dependent properties may be assembled by successive deposition of compressed monolayers formed at the water–air interface[2] (Langmuir–Blodgett monolayers[3]). Although very attractive as a means for handling molecular entities, this technique suffers from certain inherent limitations that will prevent its extension to more sophisticated systems or to large-scale applications. Development of other molecular assembling methods is therefore necessary.

Adsorption of amphipathic molecules on polar solid surfaces has been known to lead under certain conditions to formation of closely packed monomolecular films which are not wetted by organic oils (oleophobic).[4] The existing experimental evidence[5-8] points to a great similarity between the structure of such adsorbed monolayers and of Langmuir–Blodgett monolayers deposited on solid supports from the water–air interface. We have found that oleophobic monolayers containing more than one component (mixed monolayers) can also be produced by adsorption from organic solutions. The incorporation of dyes as components in such mixed monolayers renders layers subject to study by spectroscopic means. A further new development is the production of mixed monolayers containing both chemisorbed and physically adsorbed components.

The purpose of the present and the next two papers in this series is to report our first results in using adsorption on solid surfaces as a method for the production of monolayers with controllable in-plane molecular organization.

II. Adsorption of Mixed Monolayers. Wettability Observations and Desorption Properties

Three main types of mixed adsorbed monolayers were investigated: long-chain saturated fatty acids + long-chain substituted cyanine dyes,[2] *n*-octadecyltrichlorosilane (OTS–$C_{18}H_{37}SiCl_3$) + long-chain substituted cyanine dyes, and fatty acids + OTS. Mixed monolayers containing some other components, as liquid crystals, will be described in part 3. Solutions containing the active components were prepared by dilution of more concentrated stock solutions of fatty acids and dyes in chloroform and of OTS in tetrachloromethane. All solutions were adjusted to a final identical solvent composition of 8% $CHCl_3$ + 12% CCl_4 + 80% *n*-hexadecane (by volume),

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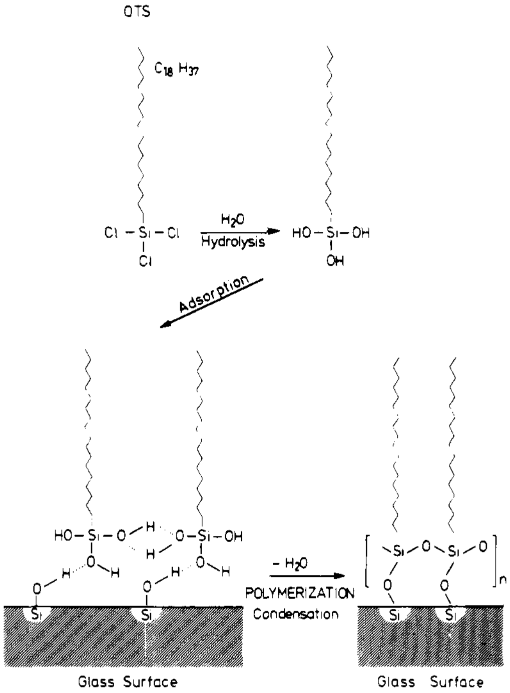
which was found optimal for the solubilization of the dyes while still maintaining a low solubility limit for the other components. Since OTS is easily hydrolyzed under the influence of atmospheric humidity and may then form undefined polymerized material (see discussion below and ref 9 and 10), the silane-containing solutions were always freshly prepared and used within 2 h after their preparation. Solid substrates which were investigated include smooth surfaces of glass, poly(vinyl alcohol), oxidized polyethylene, and evaporated aluminum. The adsorption was carried out at room temperature from 10-cm^3 glass cells by dipping the glass slides (12 × 38 mm^2) or pieces of similar dimensions cut from the other solid substrates into the organic solutions for the required period of time (see section IV), followed by a quick withdrawal. The slides were immersed and withdrawn with a velocity of about 2.7 mm/s, and the solutions were kept under continuous magnetic stirring. Details on the preparation of different surfaces and on the purification of solvents are given in the Experimental Section. An adsorbed monolayer was considered as being reasonably complete when the solid support emerged completely unwetted from the adsorbing solution.[6,7] Only complete monolayers were investigated during this work.

Unwetted pure dye monolayers (containing only dye) could not be obtained. This has probably to do with the molecular geometry of the dye which does not permit compact packing of the long-chain substituents.[4] However, in conjunction with rod-like compounds as saturated fatty acids such structures may be approached, so that oleophobic mixed monolayers of good quality are produced provided that the dye coverage does not exceed 50-60% of the monolayer area (see section IV).

The formation and properties of adsorbed monolayers depend on a number of factors, including the nature of the substrate and the nature of the adsorbed molecules. Thus, monolayers containing OTS as the main component were easily adsorbed on all substrates investigated during this work, whereas fatty acid monolayers could be formed only on glass and aluminum. Qualitative desorption and wettability observations were used in estimating the quality and stability of the monolayers. As expected, hexadecane forms droplets which move freely (without wetting the surface) on all monolayers regardless of the support or the adsorbed molecules. This behavior indicates that the outer surface consisting of closely packed methyl groups is practically the same in all cases.[4,6] Water droplets showing much higher contact angles than hexadecane move freely on OTS monolayers, regardless of the substrate, and on fatty acid monolayers adsorbed on aluminum. Water spreads on fatty acid monolayers adsorbed on glass, indicating complete desorption of the monolayer. Chloroform treatment (a few minutes at room temperature) followed by wettability observations show that the fatty acid monolayers are easily dissolved, regardless of the substrate, while OTS monolayers are completely stable under these conditions. Since the unadsorbed OTS is readily soluble in chloroform, it is apparent that the OTS molecules form very resistant structures in the adsorbed state, presumably through covalent bonding with the substrate, completed by various degrees of planar polymerization or intermolecular hydrogen bonding.

The formation of covalently bound silane monolayers on surfaces exposing free OH groups was postulated in the past,[9,11] and the following steps were assumed to be involved in this process (Scheme I). However, this simple scheme has been never supported by direct experimental evidence, most of the available experimental results indicating that thick polymeric films are adsorbed from water containing solutions which are usually employed in the adsorption of silanes.[9] The experiments discussed in section III demonstrate unequivocally that the OTS films produced by the present method are true monolayers showing quite a high degree of perfection in orientation and packing. It is reasonable to assume that with

Scheme I. Chemisorption of *n*-Octadecyltrichlorosilane (OTS) on Glass



anhydrous solutions, where water is present only as a layer adsorbed on the surface of the solid support, the silane hydrolysis cannot occur in the bulk of the liquid phase. Consequently, only OTS molecules contacting the solid surface with their polar groups are hydrolyzed. This will prevent a three-dimensional condensation of the silanol groups, favoring the formation of well-defined planar monolayers.[10] The structure assumed for the OTS monolayers in the scheme above contains elements which can explain their good quality and unusual resistance to solvent treatment. Looking at molecular models it becomes, however, clear that such a structure might be approached only in some idealized situations. It is very improbable that each OTS molecule would be able to form covalent bonds with both the substrate and its neighboring OTS molecules in a polymeric planar chain. A real structure might contain OTS molecules bonded covalently to the substrate, while forming only hydrogen bonds with adjacent OTS molecules, or vice versa. The availability of three active OH groups on each Si atom would facilitate the formation of at least one covalent bond per OTS molecule without imposing special steric restrictions. This would explain the formation of good, closely packed OTS monolayers on many types of polar substrates which may be expected to differ considerably in the density and distribution of their surface OH groups.

III. Structure Investigations by Spectroscopic Methods

The Dispersion State of the Dye Component in Mixed Adsorbed Monolayers. Seven different cyanine dyes have been employed during this work as components in various adsorbed mixed monolayers (see also part 2). Their absorption and fluorescence spectra were always typical monomeric[13] (Figure 1). Traces of dimers could be detected only at the highest possible dye concentration which still permitted the formation of oleophobic monolayers (50-60% coverage of the monolayer area). These traces are evident in the absorption spectra as a slightly increased prominence of the shoulder appearing on the short-wavelength side of the main monomeric peak. No spectral indication of higher states of aggregation could be detected. A small and gradual red shift of the absorption band is observed with increasing concentration of the dye in the monolayer, but the characteristic monomeric band shape remains

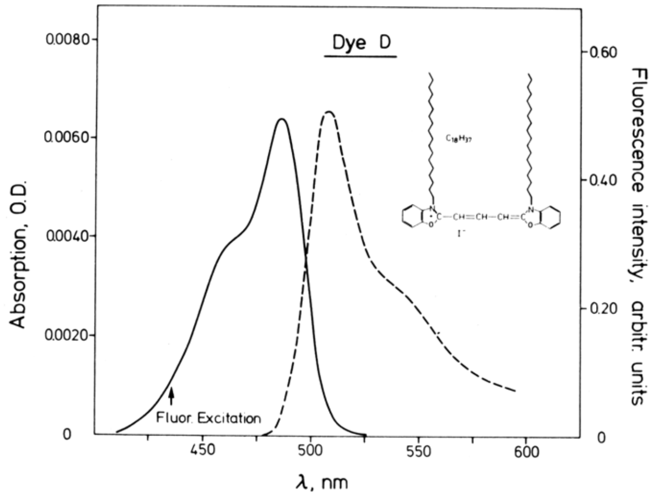


Figure 1. Monomeric absorption and fluorescence spectra of two mixed monolayers of OTS + dye D adsorbed on glass (one monolayer on each side of the slide). The molar ratio OTS/dye in the adsorbed monolayer is $R_M = 41$, and the dye coverage is 14.6% of the total monolayer area.

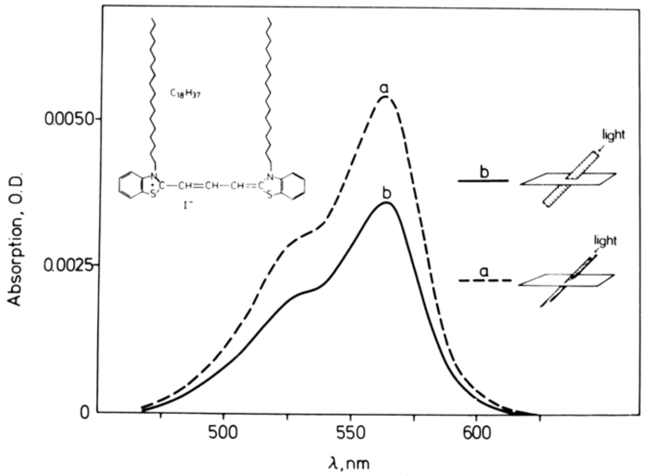


Figure 2. Typical dichroic spectrum of a mixed monolayer containing dye, adsorbed on glass. Light polarized in the layer plane (a) is absorbed more strongly than light having both in-plane and out-of-plane components of its electric vector (b). The linearly polarized light beam is incident on the slide plane at an angle of 45°.

unchanged. The maximal shift observed with dye D on going from the lowest measurable dye concentration (dye coverage ca. 1% of the monolayer area) to the highest possible concentration (ca. 60% coverage) is no more than 7–9 nm. It is therefore evident that most of the dye is adsorbed as isolated molecules. Weak intermolecular interactions become operative at high dye concentrations, without, however, leading to aggregate formation. Similar types of dye–dye interactions were described in the past in relation to adsorption of some nonaggregating dyes on grains of photographic emulsions.[14,15]

Orientation of the Dye Chromophores. The cyanine dyes employed in this work have their transition moments pointing along the longitudinal axes of the chromophores,[18] which makes it possible to determine their orientation with respect to the surface of the substrate by means of simple linear dichroism measurements.[2] Measurements with light polarized in orthogonal directions parallel to the surface show that on isotropic surfaces (like glass) the in-plane distribution of the chromophores is random. Nonrandom preferred orientations are observed in monolayers adsorbed on substrates having anisotropic surfaces (part 2). The inclination of the chromophores with respect to the substrate surface is determined by linear dichroism measurements in which the direction of polarization of the electric vector may be adjusted to scan both in-plane and out-of-plane oriented transition moments (see Figure 2). A dichroic ratio (ratio *a*/*b* in Figure 2) of 1.52 is expected for a statistical planar distribution of all moments. The very good agreement of the measured dichroic ratio (1.5) with the theoretical value demonstrates that the cyanine dye molecules are adsorbed with their chromophores parallel to the surface of the substrate (planar orientation). Cases of perpendicular orientation of the chromophores on the layer plane will be discussed in part 3 of this series.

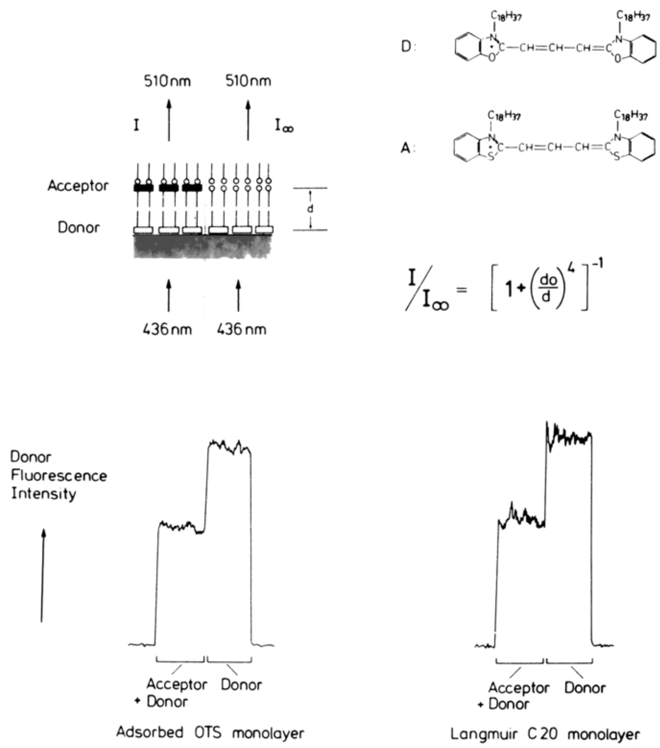


Figure 3. Energy transfer experiment used for estimating the thickness of an OTS film adsorbed on glass. The layer containing the donor dye is either a mixed adsorbed film of OTS + D or a transferred Langmuir monolayer of C_{20} + D. The acceptor layer is a transferred Langmuir monolayer of C_{20} + A. A narrow excitation light beam scans the system from left to right and the corresponding donor fluorescence is recorded. The fluorescence intensity is quenched in the sample section containing the acceptor layer (left part) to about half of its value in the section where only the donor is present (right part). Approximately the same quenching effect is observed with either Langmuir or adsorbed donor layers.

Monolayer vs. Multilayer Formation. Oleophobic fatty acid films are known to be of monomolecular thickness. Strong new support to this comes from our recent measurements of the electrical capacitance and conductivity of adsorbed fatty acid monolayers having different chain lengths.[12] With respect to OTS films, however, the possibility of multilayer formation should be carefully investigated (see section II). Another important question to be clarified is whether the dye molecules in mixed monolayers might not adsorb as multilayers on top of the first adsorbed monolayer.

The thickness of our OTS films has been determined by two independent methods: the capacitance and conductivity measurements reported in ref 12 and the energy-transfer experiments presented in the following. Both methods lead to the conclusion that these films are true monomolecular layers.

Figure 3 illustrates a Förster-type energy-transfer experiment designed such that the thickness of an adsorbed OTS monolayer may be compared with the known thickness of an arachidic acid (20 carbon atom chain, C_{20}) Langmuir monolayer.[20] The composite system consists of a mixed monolayer of OTS and a donor dye (D) adsorbed on a glass slide, on top of which a mixed Langmuir monolayer of cadmium arachidate and an acceptor dye (A) is deposited in such a manner that it covers only half of the slide area. The other half is covered by a pure cadmium arachidate monolayer, and the system is completed with a third monolayer of cadmium arachidate covering both halves of the slide. A similar system having the adsorbed monolayer replaced by a mixed C_{20} + donor dye Langmuir monolayer is assembled for comparison measurements. The transfer of energy from the donor to the acceptor dye is determined from the quenching of donor fluorescence in the part of the sample containing both the donor and the acceptor, as compared with the fluorescence in the part of the sample where only the donor is present (see Figure 3). The dependence of donor fluorescence intensity on the distance between the layers containing the donor and the acceptor chromophores is given by[2]

$$I_d/I_\infty = [1 + (d_0/d)^4]^{-1} \qquad (1)$$

where I_d and I_∞ are the fluorescence intensities for a distance d and infinity (no acceptor layer), respectively, and d_0 is the critical distance at which $I_d/I_\infty = 0.5$.

It is evident from Figure 3 that within the experimental error I_d/I_∞ is the same for both systems, which means that the respective d distances should be similar, too. Since d depends on the thickness of the superposed films, we may conclude that the adsorbed OTS film is a true monolayer having the molecular hydrocarbon chains perpendicularly oriented on the layer plane.

Strong evidence excluding the possibility of multilayer dye adsorption comes from experiments with dye monolayers oriented on anisotropic surfaces and from adsorption-desorption experiments with OTS + dye monolayers which will be reported in parts 2 and 3 of this series.

Structure Differences between Adsorbed and Langmuir Monolayers. The experimental evidence so far presented indicates that the cyanine dye molecules in mixed adsorbed monolayers are monomolecularly dispersed and have their chromophores oriented with the longitudinal axes parallel to the surface of the substrate. The orientation of the long chromophoric axes in mixed Langmuir monolayers is the same, but the aggregation state of the dye is much more complex, dimers and even higher aggregates appearing at relatively low dye concentrations.[2,21-23] The aggregation state in Langmuir monolayers depends on parameters controlling the monolayer formation at the water-air interface. At large areas/dye molecule (small surface pressure) most of the dye is in the monomeric form, whereas below a certain critical value the chromophores are forced into an edge-on position favoring the formation of sandwich-type dimers, with the chromophoric planes parallel to each other and perpendicular to the water surface[22] (see Figure 4). This structure is preserved when compressed monolayers are transferred to a solid substrate. The lack of dimerization in the adsorbed monolayers may then be interpreted as evidence that the preferred dye orientation in this case is with the chromophoric planes parallel to the surface of the substrate (flat orientation). In this orientation no sandwich-type dimers can be formed (see Figure 4). This would mean that the interaction dye-substrate with the chromophores in a flat orientation is stronger than the dye-substrate interaction with the chromophores in an edge-on position plus the dye-dye interaction due to dimer formation. This observation supports previous experimental evidence regarding the importance of the substrate in the formation of adsorbed dye aggregates, as compared with the insensitivity of Langmuir monolayer aggregates to the nature of the substrate.[21,23] One may then expect that a stable state characteristic of a certain monolayer-substrate system would be spontaneously reached only when the solute molecules are free to interact with the solid surface in the absence of external forces.

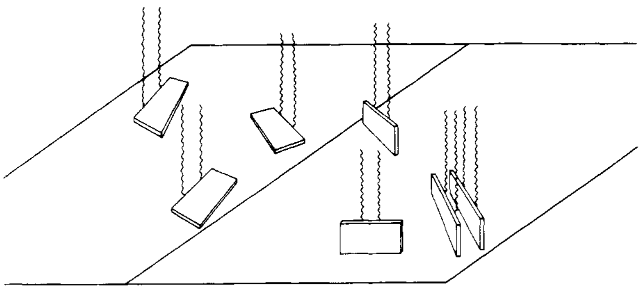


Figure 4. Schematic representation of orientation of long-chain substituted cyanine dyes with respect to a planar surface. The chromophoric planes may assume either an edge-on (right part) or a flat (left part) orientation. The longitudinal axes of the chromophores are in both cases parallel to the surface and the long paraffinic chains are perpendicularly oriented.

IV. Formation and Composition of Mixed Adsorbed Monolayers

It was previously established that with sufficiently concentrated solutions complete fatty acid or fatty amine oleophobic monolayers are formed in adsorption times ranging from a few seconds to 1 min.[4-7] A complete monolayer was considered to be attained when no change in the measured properties occurred with increasing adsorption times. This state was shown to correspond to a good close-packed arrangement of the adsorbed long-chain molecules.[4,7]

The present experiments with mixed dye monolayers were carried out under experimental conditions that ensure rapid formation of complete monolayers in the sense mentioned above. It is therefore assumed that for any adsorption time longer than 15-30 s the surface area of the substrate is completely covered by a closely packed monolayer. Accordingly, any variation in the amount of adsorbed dye (detected by absorption spectroscopy) is considered to be related to a corresponding variation in the molar ratio of the two components in the adsorbed monolayer. All experiments described in this section were performed using one representative dye, one representative fatty acid, and one representative substrate (glass slides). The mixed monolayers were C_{20} + dye D (see formula in Figure 1), OTS + dye D, and C_{20} + OTS. The surface dye concentration was calculated from absorption spectra making the reasonable assumption that the molar extinction coefficient measured in solution is not significantly changed in the adsorbed state, and correcting for the orientational effect of the chromophores at the surface. Molar ratios of the components in the adsorbed monolayers were computed from the experimentally determined dye concentrations, using the above-mentioned assumption of total surface coverage, and the following effective molecular cross sections: 170 (dye D) and 25 Å^2 (OTS and C_{20}). The area of the dye with the chromophore in a flat orientation was estimated from CPK models, as well as from X-ray data.[24] The molecular areas of C_{20} and OTS in the adsorbed monolayers were considered as being somewhat larger than in a best closely packed arrangement.[4,7,9]

Time-Dependent Experiments. Figure 5 illustrates the composition of a mixed monolayer of OTS + dye D as a function of adsorption time, for a fixed concentration and a fixed molar ratio OTS/dye D in solution, R_S. R_M is the molar ratio OTS/dye D in the adsorbed monolayer. Different points in the plot represent different slides, each one being immersed in the adsorption cell only once and for a well-defined time. The adsorption times refer to times allowed for adsorption to take place after the slides were completely immersed in the solution.[25] The order of preparation of the samples was random.

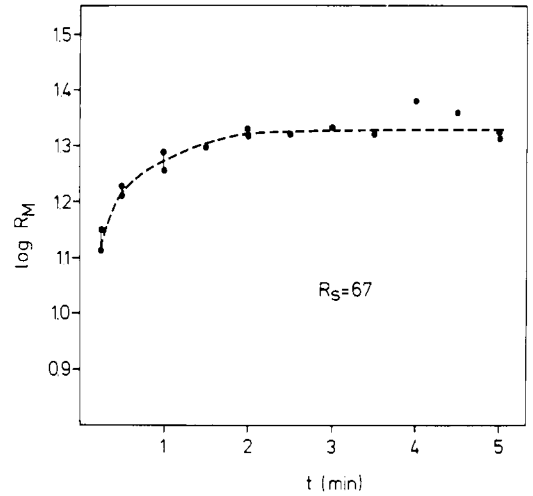


Figure 5. Varying composition of mixed OTS + dye D monolayers adsorbed on glass as a function of adsorption time: R_M and R_S are the molar ratios OTS/dye D in the monolayer and in solution, respectively.

As can be seen from Figure 5, the amount of dye in the monolayer decreases continuously (R_M increases) with increasing adsorption time, reaching a steady state after ca. 2 min. No further change in the monolayer composition occurs for longer adsorption times (samples with adsorption times of 20 min were also checked).

A completely different time dependence is shown by the pair C_{20} + dye D. Figure 6 illustrates three examples of log R_M vs. adsorption time plots obtained for two different R_S values. As before, different points represent different slides, and the order of sample preparation was random. The important common features observed in all three examples in Figure 6 is that R_M does not approach monotonically an equilibrium steady state within adsorption times of 10 min, large fluctuations occurring around some time constant mean values. It is also interesting to observe that the fluctuations characteristic of each individual adsorption time seem to be in general smaller than the fluctuations around the common mean of all points. Furthermore, the curves which were drawn by joining the mean R_M values calculated for each adsorption time show some distinct nonrandom time dependence, apparently exceeding the statistical spreading of the individual points.

A third kind of time-dependent experiments was carried out with the pair C_{20} + OTS. Wettability observations yield in this case information on the monolayer composition since a C_{20} monolayer adsorbed on glass is wetted by water, while a OTS monolayer remains perfectly hydrophobic (see section II). Both types are oleophobic to *n*-hexadecane or to their hexadecane solutions. With equimolar hexadecane solutions of C_{20} + OTS (concentration 5.0×10^{-4} M) an unwetted complete monolayer is formed in ca. 2 min. A water drop test of the monolayer reveals a nice hydrophobic behavior, which means that this is essentially an OTS monolayer. With C_{20} + OTS solutions containing C_{20} in large excess (C_{20}, 1.5×10^{-3} M; OTS, 5.0×10^{-5} M; molar ratio C_{20}/OTS 30/1) the following interesting behavior is observed. A complete oleophobic monolayer is formed in less than 30 s. This monolayer is not hydrophobic, which means that it is an essentially C_{20} monolayer. The quality of the monolayer becomes poor for adsorption times longer than 1 min, and the solution begins to leave long, wet tails on the emerging slides. An improvement in the monolayer quality is again observed with adsorption times approaching 20 min. For times above 22 min the slides emerge completely dry from the adsorption cell, and no further changes with increasing adsorption times are observed. These long-adsorption-time monolayers are nicely hydrophobic, which means that they are essentially OTS monolayers.

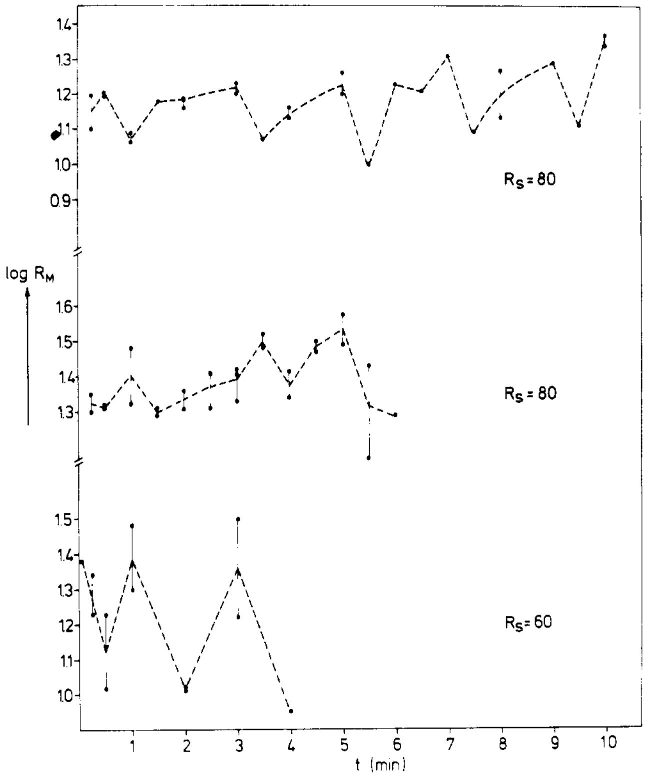


Figure 6. Varying composition of mixed C_{20} + dye D monolayers adsorbed on glass as a function of adsorption time: R_M and R_S are the molar ratios C_{20}/dye D in the monolayer and in solution, respectively. The three separate plots represent three separate sets of experiments, each performed within 2-3 h with glass slides from the same cleaning batch.

The time-dependent variations in the composition of mixed adsorbed monolayers can be rationalized only if the adsorption of the dye and of C_{20} on glass is considered to be a reversible process involving relatively weak physical forces, whereas OTS is assumed to adsorb irreversibly forming strong chemical bonds with the substrate (see section II). Physical adsorption is usually faster than chemisorption, which depends on much higher activation energies. This implies that the simultaneous adsorption of two components, one of which is physically adsorbed and the other one chemisorbed, would proceed such that the monolayer composition would be kinetically controlled (by the physical adsorption) for short adsorption times and thermodynamically controlled (by the chemisorption) for long adsorption times. This is exactly the behavior observed in Figure 5, where the dye concentration decreases with time and the molar ratio OTS/dye D approaches a final constant value for adsorption times longer than 2 min. In the case of C_{20} + OTS, good monolayers containing mostly physisorbed arachidic acid are formed very quickly, whereas stable compositions are reached only after much longer adsorption times with monolayers containing mostly chemisorbed OTS molecules. The molecular reorganization taking place at the surface while the C_{20} molecules are replaced by OTS is characterized by large imperfections and a general poor quality of the mixed monolayer. This process is evident when C_{20} is present in solution in large excess. When the solution concentrations of C_{20} and OTS are similar, the formation of a stable OTS monolayer is much quicker so that the initial formation of a monolayer containing mostly C_{20} molecules cannot be detected.

The C_{20} + dye D monolayers, where both components are physically adsorbed, are characterized by a continuous exchange with the molecules in solution. Since two different surface-active species are simultaneously present both in solution and in the adsorbed monolayer we may expect a complicated exchange process taking place at the monolayer–so-

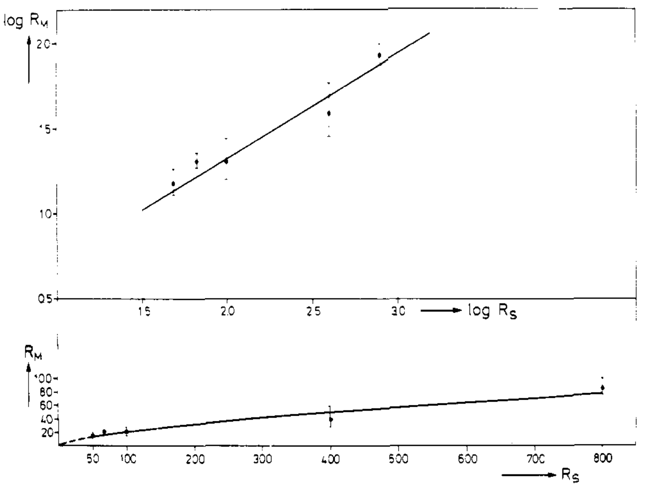


Figure 7. Stable composition of OTS + dye D monolayers adsorbed on glass vs. solution composition: R_M and R_S have the same meaning as in Figure 5.

lution interface. The behavior observed in Figure 6 would then reflect a dynamic situation where rearrangements leading to a better packing and molecular distribution within the monolayer proceed via a mechanism involving coupled interactions between the monolayer and the solution.[26] The present experimental observation of large fluctuations in the R_M values strongly supports the existence of such a dynamic state in the case of monolayers containing only physisorbed components. A critical evaluation of the exact time dependence of R_M would, however, require much more data than now available. The curves drawn through the points in Figure 6 should be therefore regarded as merely tentative.

Monolayer Composition vs. Solution Composition. An empirical functional relationship between R_M and R_S was established using stable R_M values for the (OTS + dye D)/glass system and average R_M values for the fluctuating (C_{20} + dye D)/glass system. Plots of R_M vs. R_S for these two systems are shown in Figures 7 and 8. Each point represents the average of at least ten different adsorption times between 2 and 15 min for OTS + dye D and between 1 and 15 min for C_{20} + dye A. In most cases there was more than one sample for each adsorption time. These plots are equivalent to adsorption isotherms usually employed in the treatment of adsorption data. We deal, however, with complete monolayers, so that the only variable composition parameter is in this case the molar ratio between the two adsorbed species, R_M. The range of R_S and R_M values which can be reached experimentally is subject to certain limits (see Figures 7 and 8) imposed by the limited solubility of the dye, the lowest surface concentration of the dye which can be detected spectroscopically, and the lowest C_{20} and OTS concentrations still compatible with formation of unwetted mixed monolayers.

The relationship between R_M and R_S is better grasped by plotting log R_M vs. log R_S (Figures 7 and 8, upper curves). It is then seen that a best empirical fit of the experimental points is given by a linear function of the form

$$\log R_M = a \log R_S + \log b \qquad (2)$$

This is equivalent to

$$R_M = bR^a{}_S \qquad (3)$$

The parameters a and b, determined from the slope and the intercept of the lines in Figures 7 and 8 (the upper part), are

$$a = 0.796,\ b = 0.50 \text{ (for (}C_{20}\text{ + dye D)/glass)}$$

$$a = 0.615,\ b = 1.26 \text{ (for (OTS + dye D)/glass)}$$

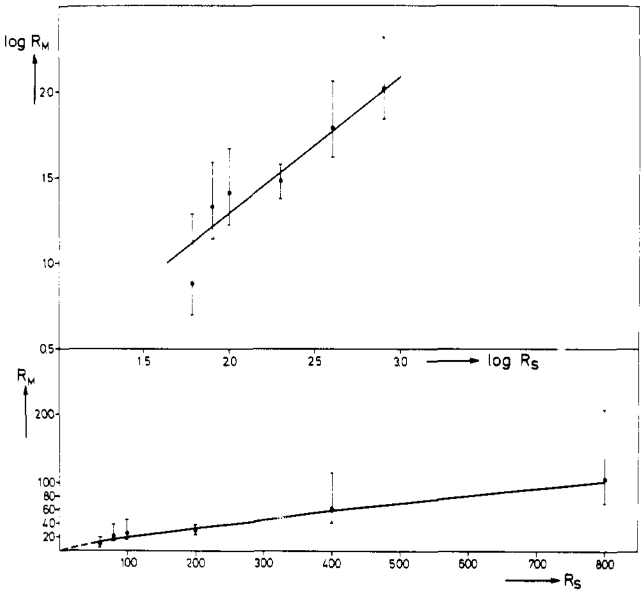


Figure 8. Average composition of C_{20} + dye D monolayers adsorbed on glass vs. solution composition: R_M and R_S have the same meaning as in Figure 6.

The curves drawn through the points in Figures 7 and 8 (lower part) are given by eq 3, with the above-determined a and b parameters.[27] The general behavior of these two systems is seen to be quite similar, except for the spreading of the experimental results, which is much greater with the pair C_{20} + dye D. This corresponds to the previously described R_M fluctuations. The smaller and random spreading of the R_M values observed with the OTS + dye D pair is most probably related to uncontrollable differences in the surface properties of individual glass slides. Although great care was devoted to a reproducible cleaning of the glass surfaces (see Experimental Section), quite large variations in the R_M values were occasionally observed even with slides from the same cleaning batch.

As can be seen from Figures 7 and 8, the experimental R_M values are always considerably smaller than the corresponding R_S. This means that the composition of the monolayer is strongly dependent on specific interactions characteristic of the adsorbed state. Different monolayer compositions may be therefore expected for different substrate–solute systems. This behavior is well illustrated with the system (OTS + dye D)/aluminum,[12] where R_M was found to be larger than the corresponding R_S ($R_S = 50$, $R_M = 120 \pm 40$). Differences in the R_M values were also observed with mixed monolayers adsorbed on the same substrate, but containing different dye components (parts 2 and 3).

V. Summary and Conclusions

It was shown that adsorption from organic solutions on polar solid surfaces can be used to produce homogeneous, compact monolayers containing more than one component (mixed monolayers). The components may be very different in their physical and chemical properties, and may have very different molecular geometries as well. The adsorption is always limited to the completion of a single monolayer adsorbed directly on the surface of the substrate. A complete monolayer is not wetted by the solution or by the pure solvent.

Either physical or chemical bonding of the adsorbed molecules to the substrate may be realized under the same experimental conditions, depending on the nature of the solute–substrate interactions. It is thus possible to produce in one step mixed monolayers containing both physisorbed and chemisorbed components.

Cyanine dyes incorporated as components in adsorbed mixed monolayers are monomerically dispersed, and oriented with the chromophores parallel to the surface of the substrate (flat orientation). This may be interpreted as evidence of chromophore-substrate interactions exceeding the energy of dye aggregation.

The formation of mixed monolayers is a dynamic process controlled by interactions involving both the molecules in the adsorbed state and those in solution. In monolayers containing only physically adsorbed components exchange with the molecules in solution takes place continuously, leading to large fluctuations in the composition of the monolayer. However, if one of the components is irreversibly adsorbed (chemisorbed), the composition of the monolayer varies smoothly and monotonically with increasing adsorption times, until a stable steady state is reached. This final stable composition, as well as the average composition characteristic of a fluctuating monolayer, is usually very different from the solution composition, being a specific function of each solute-substrate system. Any adsorption system may be thus characterized by an empirical R_M vs. R_S curve defining the composition of the monolayer as a function of the solution composition. It is important to recognize that in general not any arbitrary monolayer composition might be experimentally obtainable.

The structure and properties of mixed adsorbed monolayers make them attractive as elements for the study of induced molecular organization at well-defined solid interfaces. Applications in this direction will be presented in the next two papers of this series.

VI. Experimental Section

Preparation of the Solid Surfaces. The surface of the substrate plays an active role in the adsorption process. A proper preparation of the surface is therefore critical if monolayers having well-defined properties are to be produced. Good, defect-free monolayers are formed on very smooth and hydrophilic surfaces.

The glass slides (12 × 38 mm) used in this work were cut from glass normally used for manufacturing microscope slides, and were cleaned ultrasonically, as described below. A slide holder made of glass on which ca. ten slides can be mounted is immersed in an ultrasonic cleaning tank containing an alkaline detergent solution of Trokil 764 (Benckiser, 10 g/L) and sonicated (40 kHz) for 7 min at 100 °C. The holder with the slides is then rinsed in doubly distilled water, after which the following treatment is applied: 5 min of sonication in concentrated HNO_3 at room temperature, rinsed in doubly distilled water, 7 min of sonication in NaOH solution (5.0×10^{-3} M) at room temperature, individual washing of each slide in a jet of doubly distilled water, and finally drying in a stream of hot air (hair dryer). Sets of about 50 slides were stored without contacting each other in covered glass containers, and were used within ca. 5-10 days after the cleaning. The slides showed a nice hydrophilic behavior (water spreads) during all this time.

The preparation of aluminum supports was described in ref 12, and the preparation of polymeric surfaces is described in part 2.

Spectroscopic Measurements. The absorption and fluorescence measurements were performed with monolayer spectrometers as described by Kuhn, Möbius, and Bücher.[2] For linear dichroism measurements a rotating Glan-Thompson polarizer was placed in the light path in front of the sample. The slides were always coated with one adsorbed monolayer on each side, so that the measured spectra represent the effect due to two superposed independent monolayers.

Materials. The arachidic acid (Merck, for biochemistry) was recrystallized from an alcoholic solution. OTS (Merck-Schuchardt, for synthesis) was used without further purification. The long-chain cyanine dyes were synthesized and purified by J. Sondermann.[28] The *n*-hexadecane (Merck-Schuchardt, for synthesis) was passed twice through a column of alumina, after which it was found to be free of polar impurities according to the spreading test of Bigelow et al.[4] The chloroform and the tetrachloromethane (Baker Analyzed reagent) were passed once through a column of alumina, and the chloroform was then stabilized with absolute ethanol (1% by volume). The alumina was a Woelm-Pharma product (W 200 super I, basic).

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