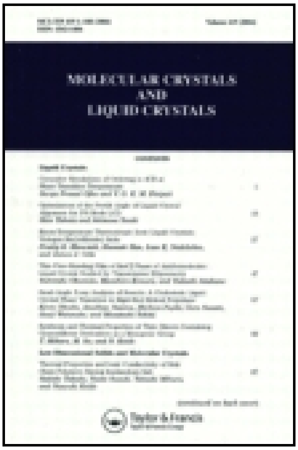

Molecular Crystals and Liquid Crystals

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Molecular Organization and Chemical Reactivity in Monolayers and Monolayer Systems

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MOLECULAR ORGANIZATION AND CHEMICAL REACTIVITY IN MONOLAYERS AND MONOLAYER SYSTEMS

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ABSTRACT The chemical reactivity of molecules in monolayers at the air-water interface is controlled by the molecular organization. Polycondensation and polymerization reactions as well as the reversible photoisomerization of a spiropyran-merocyanine system in mixed monolayers depend strongly on the applied surface pressure. The complex formation of a porphyrin in a mixed monolayer is controlled by the composition of the matrix. The limited mobility of molecules in monolayer systems requires the optimization of energy and electron transfer processes for efficient photochemical reactions.

INTRODUCTION

Many chemical or photochemical reactions require mobility of the involved molecules or molecular fragments in order to adopt the necessary relative positions and orientations or to relax to the geometry of the products. The incorporation of reactive molecules in monolayers and monolayer systems provides a unique possibility for the investigation and control of chemical reactions[1]. The molecular interactions can be manipulated by appropriate spatial and energetic coordination of the molecular components.

MONOLAYERS

The molecular organization can be controlled by variation of the monolayer composition, the composition of the adjacent bulk phases or the monolayer surface pressure. The organization of the complex monolayers at the interface consequently determines the reactivity of the molecules with reactants in the monolayer or in the adjacent bulk phase. Various chemical reactions like polycondensation[2,3], photoinduced polymerization[4], reversible photoisomerization[5] and complex formation have been studied in monolayers with respect to the influence of molecular organization.

Polycondensation and Polymerization

The aim of attempts to polymerize appropriate molecules at the air-water interface is the formation of stable ultrathin polymeric sheets. This type of structure could be extremely useful in filtration or separation processes or as insulating barrier in devices for solar energy conversion. The amine-aldehyde polycondensation has been investigated in monolayers in this context[6].

Long-chain esters of glycine and alanine form monolayers at the air-water interface. The monolayers undergo polycondensation at room temperature without any initiator or catalyst added. The polypeptide is formed leaving a monolayer of the long-chain alcohol[3]. The fraction of reacted material at the end of the reaction depends on the surface pressure under which the monolayer is kept. At small surface pressures the polycondensation is inefficient since the molecules are too far apart. At about 27 Å^2/molecule in the case of the octadecyl ester of alanine the conversion into the polypeptide reaches a maximum of 90 % and falls to 65 % at 20 Å^2/molecule[7]. The dense packing at high surface pressure is unfavorable for the polycondensation reaction, however, at medium surface pressures the molecules can optimally adapt the required geometry.

The polymerization of molecules with reactive groups at various positions has been carried out at the air-water interface[8]. The kinetics of the UV initiated polymerization of vinyl stearate monolayers at constant area per molecule has been investigated by measuring the change in surface potential during the reaction[9]. The data were fitted to a second-order rate expression. The reaction rate constant decreased with decreasing area per molecule and was at 39.6 Å^2/molecule more than three times as large as the reaction rate constant at 22.1 Å^2/molecule. This result is qualitatively in agreement with the observation that the surface pressure increases during polymerization at constant area. From the surface pressure area isotherms the extrapolated area of the monomer is obtained as 20.2 Å^2/molecule whereas the monomer unit in the polymer requires 25.2 Å^2.

The amphiphilic diacetylene compounds represent a particularly interesting class of polymerizable molecules. The study of the reactivity of various substituted diacetylenes in the solid state[10] has stimulated the synthesis of appropriate derivatives for monolayer studies. The long chain carboxylic acids with the diacetylene group in the chain, e.g. 10, 12-nonacosadiynoic acid, polymerize under UV irradiation in monolayers at the air-water interface[4]. The reaction can be followed by the appearance of the optical absorption due to the polymer in the spectral range between 500 nm and 700 nm.

The UV-initiated polymerization of the diacetylenes is a topochemical reaction, which requires a particular spatial arrangement of the monomers. Therefore, it is not observed in solution. The monolayers of amphiphilic molecules with diacetylenic groups must be compressed to the condensed phase below the phase transition temperature[11] for polymerization.

Matrix-controlled Complex Formation

The complex monolayers formed of different components offer a new dimension of control compared with monolayers of a single molecular species: the monolayer composition. The reacting species may be incorporated in the matrix of unreactive molecules which provide a means of environmental control. An example is the metallation of an amphiphilic free base porphyrin in a mixed monolayer of the porphyrin (PO), methylarachidate (AME) and arachidic acid (C20). The composition of the monolayer is varied by changing the ratio of ester to acid, leaving the fraction of the porphyrin constant.

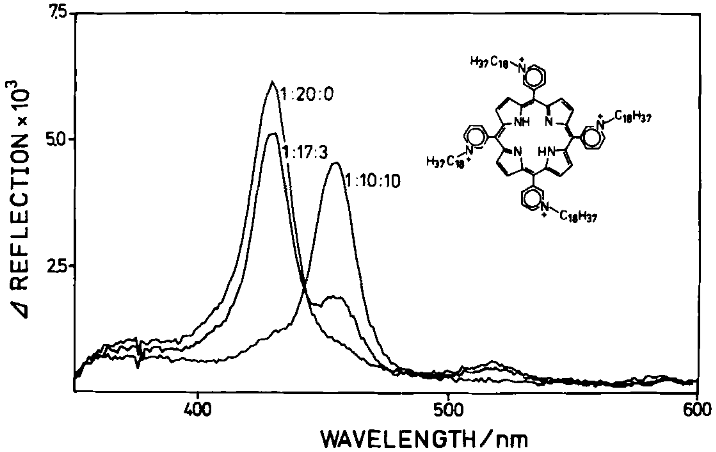

FIGURE 1: Spectra of the enhanced light reflection from the surface of an aqueous solution of 10^{-6}M $CdCl_2$ and 5×10^{-5}M $NaHCO_3$ for three mixed monolayers of the amphiphilic porphyrin (PO), methylarachidate (AME) and arachidic acid (C20) of the composition (molar ratios) of PO:AME:C20 indicated at curves.

The monolayers are formed on an aqueous solution of cadmium chloride (10^{-6}M) and sodium bicarbonate (5×10^{-5}M). The light reflection from the water surface is increased in the presence of a monolayer in the spectral region of the monolayer absorption. The spectrum of this additional light reflection (see Fig. 1) shows the Soret band of the free base phorphyrin at 430 nm in the case of the monolayer composition (molar ratios) PO:AME: C20 = 1:20:0 and the shifted Soret band at 455 nm of the cadmium complex of the porphyrin in the case of monolayer composition PO:AME:C20 = 1:10:10. A spectrum with both Soret bands is obtained in the case of PO:AME:C20 = 1:17:3[12]. The molecular structure of the porphyrine PO is given in Fig.1.

It can be concluded from absorption measurement of transferred monolayers with linearly polarized light that the porphyrin ring lies flat on the water surface. The four long chain substituents occupy only about 80 $\AA^2$/PO molecule in the mixed monolayers, and the space above the flat chromophore is filled with matrix molecules. The porphyrin molecule carries four positive charges. The approach and incorporation of the divalent cadmium cation is inhibited without compensation by negative charges in the monolayer. Complete formation of the complex is observed with monolayers containing excess arachidic acid in addition to charge compensation of the porphyrin. The diffusion layer underneath the monolayer is controlled by the composition of the monolayer matrix. The fraction of cadmium complex can be determined from the spectra. A "titration curve" is obtained plotting this fraction against the molar ratio of arachidic and porphyrin in the monolayer with the midpoint at 4 molecules arachidic acid per porphyrin molecule[12].

Photoisomerization

Photoisomerization reactions in monolayers lead to changes in the area per molecule at constant surface pressure, in surface potential, and in spectroscopic properties. The photochromic system of an amphiphilic anthocyanidine has been studied in monolayers at the air-water interface by measurement of the change in surface potential[5]. The rate constant of the dark reaction (opening of the ring) depends on the pH of the aqueous subphase[5]. Cis→trans photoisomerizations have been observed in monolayers but no trans→cis isomerization[1]. This is plausible, since the cis-isomer has a larger area per molecule in the systems studied.

Spectral changes during photoisomerization reactions in monolayers can easily be followed and the involved species identified by measurement of the light reflection from the water surface. This method has been applied to the study of an amphiphilic spiropyran(SP)-merocyanine (MC) system in mixed monolayers at the air-water interface[13]. A monolayer of the spiropyran and octadecanol(C18OH), molar ratio SP:C18OH = 1:5, shows no enhanced light reflection in the visible spectrum (see Fig. 2). On irradiation with UV radiation (366 nm) the merocyanine is formed. At constant surface pressure of 10 dyn/cm the area increases by about 50 % of the initial area. The reflection spectrum picked up from the water surface then shows a pronounced band with maximum at 620 nm which is typical for the merocyanine MC.

The merocyanine can be reacted back into the spiropyran by irradiation with visible light (545 nm). The matrix of octadecanol provides sufficient flexibility for both photoreactions to occur in the SP-MC system. In a matrix of stearic acid on water the rate constant of the photoreaction SP→MC at constant surface pressure π decreases nearly linearly with increasing π from $0.03\ s^{-1}$ at π = 5 dyn/cm to $0.013\ s^{-1}$ at π =

15 dyn/cm, and then stays constant. The reaction is slowed down with increasing surface pressure due to a higher microviscosity of the reacting molecules.

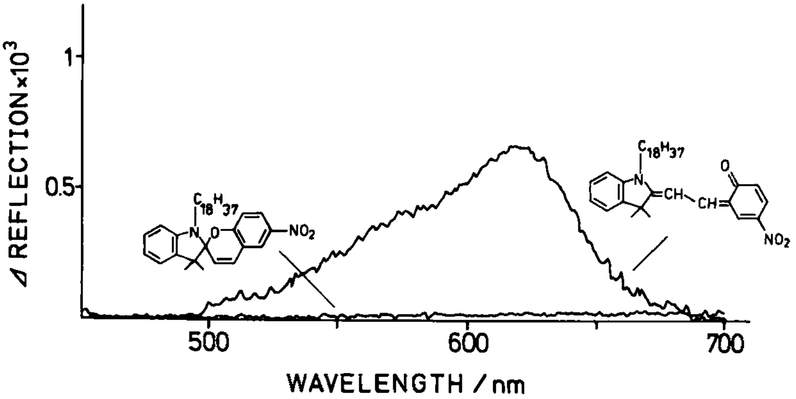

FIGURE 2. Reflection spectra from a mixed monolayer of the spiropyran-merocyanine system and octadecanol, molar ratio 1:5, before (lower trace) and after photoisomerization with UV radiation (upper trace) at a surface pressure of 10 dyn/cm.

This photochromic system offers an interesting application. The surface pressure at constant area increases rapidly on flash exposure, followed by some slow relaxation. A monolayer of a cyanine dye with a phase transition from monomeric to aggregated state at π = 7 dyn/cm in contact with the photochromic monolayer can be reorganized by flash exposure of the spiropyran[13]. The fast rise of π provides a 2-dimensional pressure jump, with the possibility of studying relaxation phenomena in complex monolayers.

MONOLAYER SYSTEMS

Organized systems of monolayers can be assembled, adopting the Langmuir-Blodgett technique[14], by stepwise transfer of the different complex monolayers from the water surface to a solid substrate. In this way the control of molecular organization at the air-water interface can be used for the construction of planned monolayer systems. A different way of growing layered structures on a solid in a sequence of surface chemical reactions is being developed[15]. This technique has some advantages compared with the Langmuir-Blodgett method: no need of a water surface, the final film structures are thermodynamically equilibrated with no mechanical manipulation of the film.

Molecular Mobility

The microviscosity of molecules in monolayer systems depends strongly on the monolayer composition and details of monolayer preparation and transfer. In a sequence of manipulations a dye monolayer has been reorganized by interaction of the chromophores with an anisotropic solid surface introducing a preferential orientation. The monolayer was then removed from this solid and transferred via the water surface onto a glass plate without change in the introduced orientation of the chromophores[16]. This experiment demonstrated that the mobility of molecules or molecular fragments in monolayer systems can also be controlled.

Diffusion of small molecules or ions across monolayers has been observed[1]. However, the penetration of ions into monolayer systems from an adjacent aqueous solution can be prevented. The penetration of Cu^{2+} ions is easily detectable since these ions quench the fluorescence of excited cyanine dyes by electron transfer. In Fig. 3 the fluorescence intensity of a cyanine dye incorporated into a monolayer of arachidic acid in a mole fraction of 1/100 is plotted against time after addition of $CuCl_2$ into the aqueous substrate in contact with the monolayer systems (structures schematically shown). The concentration of Cu^{2+} was 10^{-5} M. In the case of the lower structure with the fluorescence probe exposed directly to the Cu^{2+} solution the fluorescence intensity drops immediately to about 1/5 of the initial va-

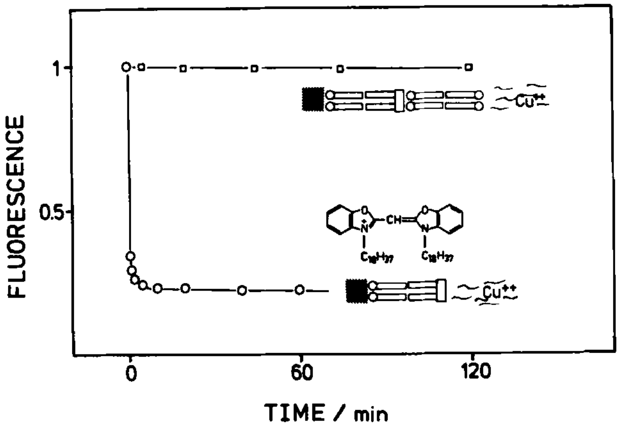

FIGURE 3. Fluorescence intensity of the probe cyanine incorporated in an arachidate matrix (mole fraction of dye 1/100) against time after addition of $CuCl_2$ into the aqueous substrate. Probe monolayer exposed directly to the solution (circles): strong quenching. Probe monolayer protected by 2 cadmium arachidate monolayers (squares): no quenching and therefore no penetration of Cu^{2+}.

lue. When the monolayer with the probe is protected by two monolayers of cadmium arachidate (upper structure in Fig. 3), essentially no change in fluorescence intensity is observed within 2 h. Thus, no detectable penetration of Cu^{2+} has occurred.

Energy and Electron Transfer Processes

In rigid monolayer systems the reorganization of molecules in the course of a chemical reaction is nearly impossible. This causes the small quantum yields of photoisomerization and of photoelimination reactions in these systems[1]. For bimolecular or polymerization reactions the molecules have to be in the appropriate positions and orientations like in topochemical solid state reactions. Limited formation of cyclobutane photodimers has been observed[1].

The fascinating polymerization of diacetylene type compounds has also been carried out in monolayer systems[17]. The polymerization proceeds across domains of the character of two-dimensional crystals[18]. The reaction can be sensitized to visible light by incorporation of cyanine dyes in adjacent monolayers. The sensitization mechanism includes electron and energy transfer processes[19].

Energy and electron transfer processes do not require large changes in the molecular geometry, and the monolayer systems are particularly suited for systematic studies of these processes[16]. The photoinduced electron transfer from an excited donor to an electron acceptor in the adjacent monolayer can be investigated by measuring the quenching of the donor fluorescence. The electron returns from the reduced acceptor to the ground state orbital of the donor if no secondary reactions occur which may lead to stable products. The role of energy delocalization in the donor monolayer has been studied in order to optimize the primary step.

When the mole fraction of the dye in the mixed donor monolayer is very small (e.g. molar ratio of dye to matrix molecules 1:1000) the average distance between donor molecules is too large for donor-donor energy transfer to occur. The relative fluorescence intensity I/I_o of the donor monolayer (I in presence, I_o in absence of the acceptor) should decrease exponentially with increasing density of acceptor molecules in the adjacent monolayer according to a hard disk model of electron transfer[20]:

$$I/I_o = \exp\ (-\pi\ r_{DA}^2\ \sigma_A)$$

where r_{DA} is the critical radius for electron transfer and σ_A the density of acceptor molecules. This dependance is indeed observed.

At higher donor density in the mixed donor monolayer the excitation energy is delocalized due to Förster energy transfer between donor molecules. Consequently, the electron acceptor becomes more efficient since the excited state that would have been deactivated by fluorescence emission can now arrive at donor molecules within the critical radius of an acceptor molecule. This effect is shown in Fig. 4 for monolayer systems with the indicated donor and acceptor molecules arranged at the same

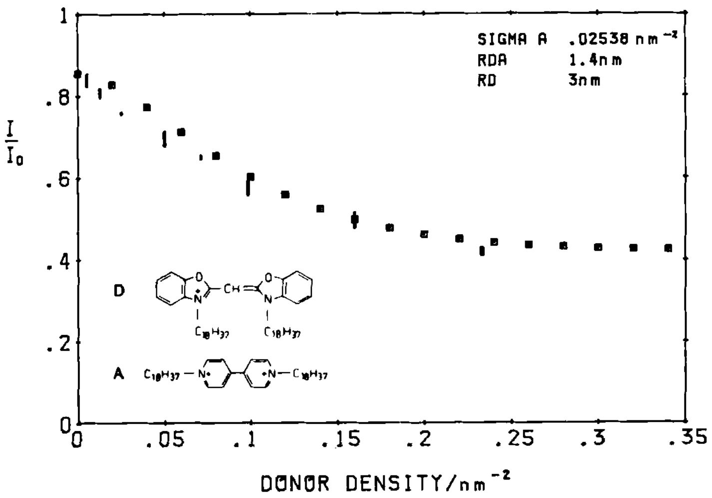

FIGURE 4. Relative donor fluorescence intensity plotted against the donor density in a monolayer system with donor D and acceptor A (structures indicated) arranged at the same interface. Experimental results: bars; calculated values with a model including donor-donor Förster energy transfer: squares. The parameters given are the critical radii for electron transfer (r_{DA}) and energy transfer (r_D), and the fixed acceptor density.

interface. The relative fluorescence intensity is plotted against the donor density (bars) and compared with the result of a model[20] including Förster energy transfer between donor molecules (squares).

The delocalization of the excited state in a dye monolayer can be optimized by improving the packing of the chromophores. Strong dye-dye interactions are observed in large arrays of chromophores, the J-aggregates[21]. Indeed, the electron acceptor is most efficient in contact with the aggregate of the cyanine[22]. In Fig. 5 the product

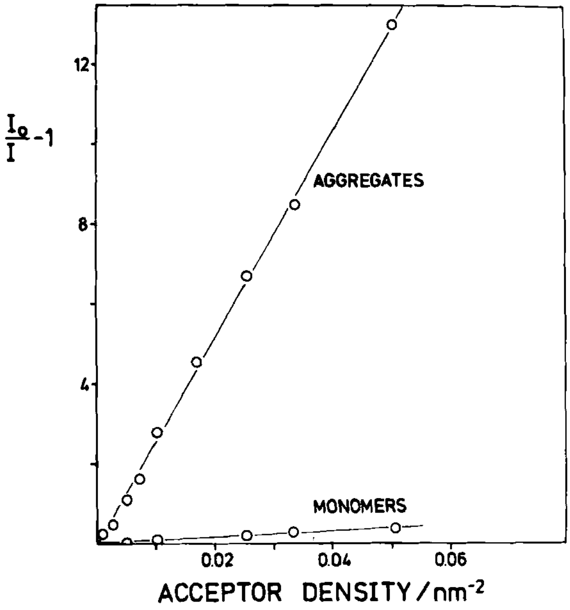

FIGURE 5. Plot of $(I_o/I)-1$ against the acceptor density in the adjacent monolayer. The experimental results refer to donor monolayers organized as monomers without donor-donor interactions and as J-aggregates, respectively. Structures of the donor and the acceptor as in Fig. 4.

$v_{DA}\tau$ of the average rate of the electron transfer and the lifetime of the excited state as calculated from the relative fluorescence intensity, $(I_o/I)-1$, is plotted against the acceptor density. The two sets of experimental results correspond to donor monolayers without any donor-donor interaction(monomers) and to monolayers of J-aggregates of the cyanine dye (dye and acceptor structures as in Fig. 4). From the figure it is evident that $v_{DA}\tau$ is larger by a factor of 30 in the case of aggregates than for monomers. Since the lifetime of the excited state of the aggregate is smaller by at least a factor of 20 than that of the monomers, the rate for photoinduced electron transfer v_{DA} is increased by a factor of more than 600 by appropriate molecular organization.

CONCLUSION

The chemical reactivity in complex monolayers at the air-water interface can be controlled externally by the various parameters influencing the molecular organization. In monolayer systems, the desired reaction pathway can be favored by optimization of the relevant molecular interactions like energy and electron transfer.

REFERENCES

1. D.G. Whitten, Angew. Chem. internat. Edit. 18, 440 (1979).
2. T. Folda, L. Gros and H. Ringsdorf, Macromol. Chem., Rapid Commun. 3, 167 (1982).
3. K. Fukuda, Y. Shibasaki and H. Nakahara, J. Macromol. Sci.- Chem. A15, 999 (1981).
4. D.R. Day, H.H. Hub and H. Ringsdorf, Isr.J. Chem. 18, 325 (1979; D.R. Day, J.B.Lando and H. Ringsdorf, Ordering in Two Dimensions, edited by S. K.Sinha (North Holland, New York 1980), p. 455.
5. D. Möbius, H. Bücher, H. Kuhn and J.Sondermann, Ber. Bunsenges. phys.Chem. 73, 845 (1969)
6. S.J. Valenty, Macromolecules 11, 1221 (1978).
7. K. Fukuda, Y. Shibasaki and H. Nakahara, Thin Solid Films, in print 1983.
8. For a recent review see M. Breton, J. Macromol.Sci. - Rev. Macromol. Chem. C21, 61(1980).
9. S.A. Letts, T. Ford, jr. and J.B. Lando, J. Coll. Interface Sci. 56, 64 (1976).
10. G. Wegner, Pure Appl. Chem. 49, 443 (1977).
11. H.H. Hub, B. Hupfer, H. Koch and H.Ringsdorf, J. Macromol. Sci. - Chem. A15, 701 (1981)
12. H. Grüniger and D. Möbius, publ. in preparat.

13. H. Grüniger and D. Möbius, unpubl.
14. K.B. Blodgett and I. Langmuir, Phys. Rev. 51, 964 (1937).
15. L. Netzer and J. Sagiv, J. Am. Chem. Soc.,in print.
16. D. Möbius, Acc. Chem. Res. 14, 63 (1981).
17. J.P. Fouassier, B. Tieke and G. Wegner, Isr. J. Chem. 18, 227 (1979);B. Tieke and G. Lieser, J. Coll. Interf. Sci. 83, 230 (1981).
18. G. Lieser, B. Tieke and G. Wegner, Thin Solid Films 68, 77 (1980).
19. C. Bubeck, B. Tieke and G. Wegner, Ber.Bunsenges. Phys. Chem. 86, 499 (1982).
20. D. Möbius, publ. in preparation.
21. H. Bücher and H. Kuhn, Chem. Phys. Lett. 6, 183 (1970); D. Möbius and H. Kuhn, Isr. J. Chem. 18, 375 (1979).
22. D. Möbius, Mol. Cryst. Liq. Cryst. 52, 235 (1979).