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(25) Remark made by the referee.

Studies on Monolayers. 1. Surface Tension and Absorption Spectroscopic Measurements of Monolayers of Surface-Active Azo and Stilbene Dyes

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Abstract: In order to develop new molecules as functional components of monolayer assemblies a series of nine surface-active azo and stilbene compounds are synthesized. Their monolayer properties at the air-water interface are studied by surface pressure–surface area measurements and spectroscopic techniques. The results show that small changes in the molecular structure of the surfactants (such as, e.g., length of the fatty acid chain, type of the chromophore) have an immense influence on the monolayer properties. For monolayers of compounds I and III–VIII, van der Waals-like isotherms are obtained, which show a liquid expanded state, a phase transition region, and a condensed state. From monolayer absorbance spectra it is found that in the liquid expanded state at 100–110 Å^2/molecule the chromophores lie flatly on the water surface, forming monomers. As concluded from surface absorbance–surface area isotherms the phase transition region of the isotherms can be assigned to a change of orientation of the chromophore axis (horizontal → vertical) and an aggregation process of the chromophores (monomers → H aggregates). High dichroic and narrow absorbance bands are observed for condensed films of dyes VI and IX, which are assigned to H aggregates (planar pincushion-like arrangement of the chromophores). By means of molecular CPK models several molecular arrangements are discussed which are consistent with the experimental results.

Introduction

In the last few years there has been an increasing interest in the use of surface-active dyes to study properties of biological and artificial membranes and to construct monomolecular systems by self-organization.[1-6] The majority of dye molecules used for this field consists of hydrophilic chromophores, which are convalently bound to long-chain paraffins. When these dyes are incorporated into lamellar systems, it is found that the paraffin chains stand perpendicularly on the plane of the layer while the chromophores lie flat near the hydrophilic interface. It would be desirable to realize monolayer assemblies with chromophores of which the molecular long axis is oriented perpendicular to the plane of the layer. Chromophores in this arrangement should be useful as dye probes for biomembrane research, e.g., as transmembrane electric field indicators and as functional components of monolayer assemblies. For this reason the surface-active dyes I–IX were synthesized and their surface-active behavior at the air–water interface was studied by determining surface pressure–area isotherms and linearly polarized absorption spectra. Several points which lead to the design of these molecules should be mentioned.

(1) In order to possess lipid properties, the chromophore should be attached to a lipid, e.g., fatty acid or monoglyceride.

(2) The chromophore must be sufficiently hydrophobic in order to be lifted up easily from the water surface at relatively low surface pressures.

(3) The chromophore must be almost as long as the lipid backbone to reduce environmental perturbation in the lamellar system.

(4) The absorption and the emission spectra of the chromophores should depend on the polarity of their environment.

(5) In the visible region of light there should be a strong π–π transition, the polarization of which, in relation to the geometry of the molecule, must be known.

The azo and stilbene chromophores, described here, satisfy these criteria.[7]

Experimental Section

General. Melting points were obtained on a Mettler FP2 apparatus and are uncorrected. Elemental analyses were performed by Microlab. Beller, Göttingen. For column chromatography silica gel 60 (Merck, Darmstadt) was used. Mass spectra were recorded on a Varian MAT 311. NMR spectra were determined in CDCl$_3$ solutions with tetramethylsilane as a reference on a Bruker WH 270. Splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet, m, multiplet; br, broad and no line separation, respectively.

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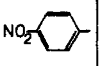
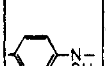
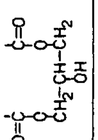
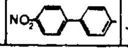
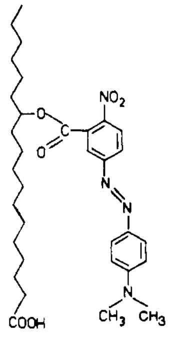
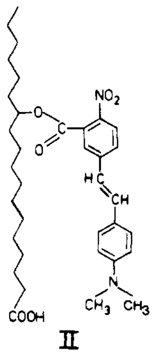
Table I. Chromophoric Diglyceride Derivatives

dye	aromatic group II	linkage group	aromatic group I	spacer group	long-chain hydrocarbon	hydrophilic portion
III		$-N{=}N-$		$-[CH_2]_5-$	$CH_3-[CH_2]_{18}-$	
IV					$CH_3-[CH_2]_{14}-$	
V				$-[CH_2]_2-$	$CH_3-[CH_2]_{18}-$	
VI					$CH_3-[CH_2]_{14}-$	
VII		$-HC{=}CH-$		$-[CH_2]_5-$	$CH_3-[CH_2]_{16}-$	
VIII				$-[CH_2]_2-$	$CH_3-[CH_2]_{14}-$	
IX		$-N{=}N-$			$CH_3-[CH_2]_{16}-$	

1. Synthesis of Chromophoric Stearic Acid Derivatives (Dyes I and II). Preparation of 12-Iodostearic Acid. Methyl 12-hydroxystearate was obtained by alkylation of 12-hydroxystearic acid (Fluka, Buchs, Switzerland) with dimethyl sulfate in the usual way and purified as described previously.[8] After recrystallization from methanol, mp 54.0–55.5 °C (lit. 57–58 °C),[9] 9.4 g (0.03 mol) of methyl 12-hydroxystearate was dissolved in 100 mL of anhydrous carbon disulfide and 0.6 g (0.02 mol) of red phosphorus was added. The resulting suspension was stirred at room temperature and a solution of 4 g (0.032 mol) of iodine in 50 mL of carbon disulfide was added dropwise. The mixture was stirred for 4 h at 40 °C. The red phosphorus was filtered off, the filtrate evaporated, and the residue dissolved in chloroform and washed several times with ice water. The chloroform was removed and the remaining oil taken up in 50 mL of ethyl alcohol and 50 mL of concentrated HCl. The resulting mixture was refluxed for 24 h. The dark brown solution was clarified by reducing the free iodine with thiosulfate. The mixture was extracted with ether and the organic layer was dried (Na_2SO_4), treated with charcoal, and evaporated to leave 8.6 g (70%) of 12-iodostearic acid (pale yellow oil) which was crystallized from methanol, mp 32–34 °C. Only few impurities were indicated by thin layer chromatography. Anal. Calcd for $C_{18}H_{35}O_2I$ (410.33): C, 52.81; H, 8.62; O, 7.81; I, 31.00. Found: C, 52.98; H, 8.78; O, 7.70; I, 30.25.



I



II

Preparation of 4′-Nitro-4-dimethylaminoazobenzene-3′-carboxylic Acid. 3-Amino-5-nitrobenzoic acid (18.2 g, 0.1 mol) (Aldrich-Europe) dissolved in a mixture of 150 mL of acetic acid and 40 mL of concentrated HCl was diazotized at 6 °C with 14 g (0.12 mol) of pentyl nitrite and coupled with 12 g (0.1 mol) of dimethylaniline (dissolved in 40 mL of acetic acid). After the coupling reaction, aqueous sodium acetate solution was added (pH 2.5). After 2 h the red precipitate was filtered, dried, and recrystallized from ethanol. The dark red product was obtained in 65% yield, mp 183–184 °C. Anal. Calcd for $C_{15}H_{14}N_4O_2$ (314.3): C, 57.31; H, 4.50; N, 17.83; O, 20.36. Found: C, 57.41; H, 4.68; N, 17.93; O, 20.43.

Preparation of the Silver Salt (Ia). 4′-Nitro-4-dimethylaminoazobenzene-3′-carboxylic acid (3.5 g, 10 mmol) and 2 g (25 mmol) of sodium acetate were pulverized and dissolved in 200 mL of hot ethanol. The solution was refrigerated overnight and the precipitated sodium salt of the azo dye was filtered off, washed with cold ethanol, and dissolved in water. An aqueous silver nitrate solution was added. The precipitated silver salt (Ia) was filtered, washed with dry acetone, and dried over KOH under vacuum.

Preparation of 12-(4′-Nitro-4-dimethylaminoazobenzene-3′-carboxyloxy)stearic Acid (Dye I). Freshly prepared dry silver salt Ia (2.6 g, 6 mmol) was suspended in 20 mL of anhydrous benzene and 2 g (6.5 mmol) of 12-iodostearic acid was added. The mixture was stirred at 30 °C for 30 h and filtered. The organic solvent was evaporated and the residual oil taken up in light petroleum. By treating the solution with dry hydrogen chloride the protonated azo dye precipitated. The petroleum, which contained residual 12-iodostearic acid, was decanted. The protonated azo dye was dissolved in chloroform, washed with water, in order to deprotonate the dye, dried with Na_2SO_4, and evaporated. The residual red oil was purified two times by silica gel column chromatography. In the first column the dye was eluted with benzene/ethyl acetate/acetic acid (6:1:1). The main fraction was pooled and applied to a second column containing silica gel and benzene/ethanol (12:1). The best fractions were again pooled, the solvent was evaporated, and the residual oil was crystallized in cyclohexane. The yield was 116 mg of dark red crystals. The solid crystals changed to liquid drops in the temperature range of 60–70 °C, which probably indicates liquid-crystal-like behavior. Anal. Calcd for $C_{33}H_{48}O_6N_4$ (596.8): C, 66.42; H, 8.11; N, 9.39; O, 16.09. Found: C, 66.54; H, 8.12; O, 16.15. Mass spectrum: *m/e* 596 (M^+).

A small amount of dye I was hydrolyzed. The resulting hydroxystearic acid was identical with the hydrolyzed methyl 12-hydroxystearate (sharp melting point of a mixture of the two acids).

Preparation of 2-Nitro-5-methylbenzonitrile. 2-Nitro-5-methylbenzonitrile was prepared by nitration of *m*-tolyl cyanide using the procedure previously described.[10]

Preparation of 4′-Nitro-3′-cyano-4-dimethylaminostilbene (Trans Isomer).[13] A mixture of 6.5 g (40 mmol) of 2-nitro-5-methylbenzonitrile, 5.5 g (50 mmol) of 4-dimethylaminobenzaldehyde, and 10 drops of piperidine was heated for 2 h at 140 °C. A red solid cake was formed during the reaction. The solid product was dissolved in 30 mL of hot ethanol. The solution was refrigerated overnight. Red crystals precipitated which were filtered off. The yield of the crude product was 5.2 g (45%). Recrystallization from dioxane gave mp 219.5 °C. Anal. Calcd for $C_{17}H_{15}N_3O_2$ (293.35): C, 69.60; H, 5.16; N, 14.33; O, 10.91. Found: C, 69.73; H, 5.20; N, 14.38; O, 10.77.

Preparation of 4′-Nitro-4-dimethylaminostilbene-3′-carboxylic Acid (IIa). A two-step hydrolysis of the cyano compound led to the desired product.

A. A mixture of 3 g (10 mmol) of 4′-nitro-3′-cyano-4-dimethylaminostilbene, 50 mL of ethanol, 5 mL of water, and 1 g of sodium hydroxide was refluxed for 10 h. The mixture was diluted with water and neutralized with acetic acid. Red crystals of the amide precipitated and were filtered off. Recrystallization from dioxane gave mp 237.5 °C. Anal. ($C_{17}H_{17}N_3O_3$) C, H, N.

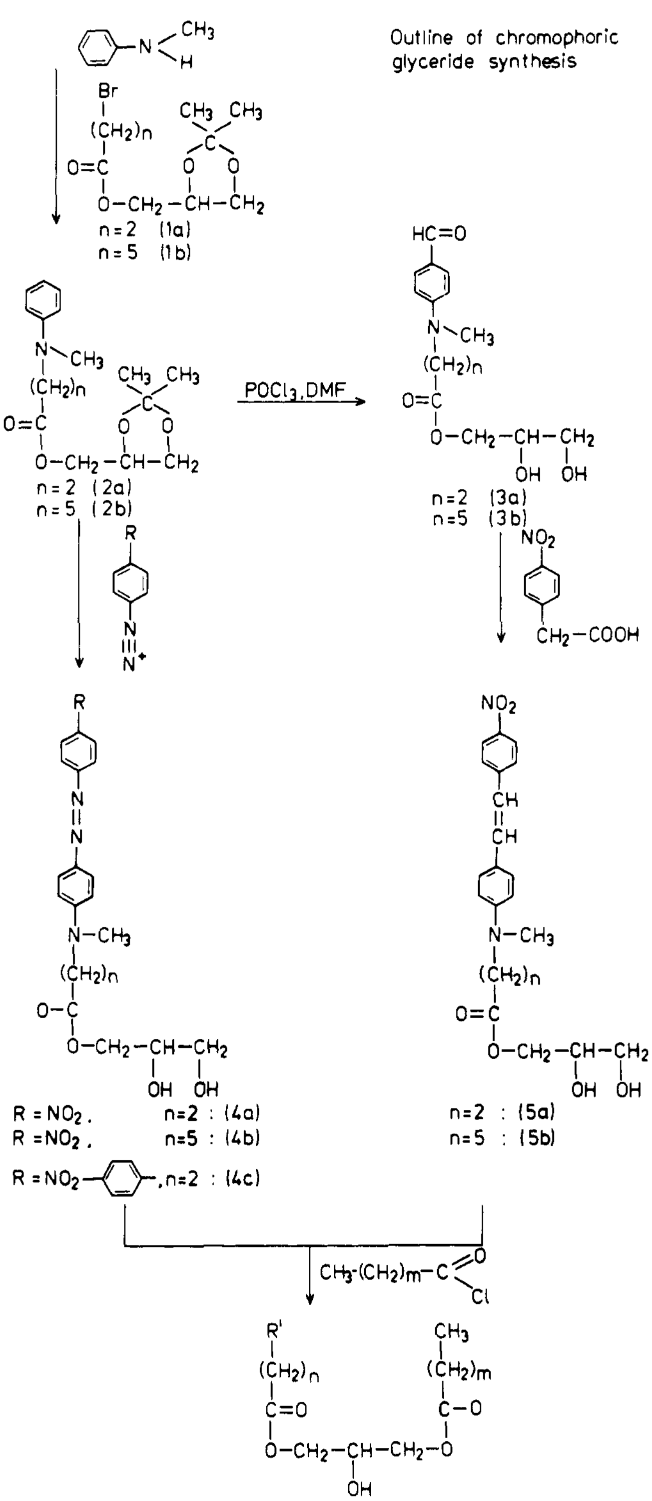
B. A mixture of 3.1 g (10 mmol) of amide, 50 mL of concentrated HCl, and 20 mL of glacial acetic acid was refluxed for 10 h. The solution was poured into a hot aqueous solution of sodium acetate. After cooling, red crystals precipitated. They were recrystallized from glacial acetic acid, mp >301 °C. Anal. Calcd for $C_{17}H_{16}N_2O_4$ (312.33): C, 65.38; H, 5.16; N, 8.97; O, 20.49. Found: C, 65.42; H, 5.22; N, 8.90; O, 20.38.

Preparation of 12-(4′-Nitro-4-dimethylaminostilbene-3′-carbonyloxy)stearic Acid (II). The preparation of the silver salt failed because of decomposition. For that reason the preparation of II was carried out through the reaction of the triethylammonium salt (IIa) with 12-iodostearic acid. The preparation and purification procedure was the same as described for I (yield 8%). Recrystallization from petroleum ether gave mp 66.7–67.8 °C. Anal. Calcd for $C_{35}H_{50}N_2O_6$ (594.76): C, 70.71; H, 8.48; N, 4.71; O, 16.16. Found: C, 70.80; H, 8.53; O, 16.05. Mass spectrum: *m/e* 594 (M^+).

Synthesis of Chromophoric Diglycerides. Preparation of 2,3-*O*-Isopropylideneglycerol. 2,3-*O*-Isopropylideneglycerol was prepared according to the method of ref 11.

Preparation of (2,3-*O*-Isopropylidene)propyl 3-Bromopropionate (1a). To a mixture of 12 g (0.15 mol) of pyridine, 13.5 g (0.1 mol) of 2,3-*O*-isopropylideneglycerol, and 100 mL of chloroform a solution of 17 g (0.1 mol) of 3-bromopropionyl chloride in 20 mL of chloroform was added slowly with stirring and cooling and stirring was continued for 5 h at room temperature. The mixture was washed with water and 0.5 N citric acid to remove the pyridine, dried (Na_2SO_4), evaporated, and fractionated, bp 82–90 °C (0.1 mmHg).

Preparation of (2,3-*O*-Isopropylidene)propyl 6-Bromohexanoate (1b). The preparation procedure of **1a** was used (acylating reagent 6-bromohexanoyl chloride).



Preparation of (2,3-*O*-Isopropylidene)propyl 6-(*N*-Methylanilino)propionate (2a). **1a** (13 g, 0.05 mol) and 15 g (0.14 mol) of *N*-methylaniline were stirred at 40 °C for 4 days, cooled, diluted with 100 mL of chloroform, and washed with an aqueous solution of 10% $NaHCO_3$ and water. The organic phase was dried (Na_2SO_4) and the chloroform evaporated. The excess of *N*-methylaniline was removed by distillation (bath, t = 60 °C, pressure = 0.5 Torr). The residue (dark brown oil) was the crude product **2a**, which was further purified by column chromatography (silica gel, ethyl acetate). Anal. Calcd for $C_{16}H_{23}NO_4$ (293.2): C, 65.54; H, 7.86; O, 21.81. Found: C, 65.41; H, 8.00; O, 21.72.

Preparation of (2,3-*O*-Isopropylidene)propyl 6-(*N*-Methylanilino)hexanoate (2b). Compound **2b** was prepared in the way described for **2a.**

Preparation of 1-[*N*-(4′-Nitro-1′-phenylazo-*p*-phenyl)-*N*-methylaminopropionyl]glycerol (4a). 4-Nitroaniline (1 g, 7 mmol) was dissolved in 10 mL of concentrated HCl, cooled to 5 °C, diazotized with 500 mg (7 mmol) of $NaNO_2$ in 2 mL of water, and coupled with 2 g (0.68 mmol) of **2a.** After the red solution was stirred for 30 min an aqueous sodium acetate solution was added to pH 4. The red precipitate was filtered off, dried, and further purified by column chromatography (silica gel, ethyl acetate), mp 111–112 °C. Anal. Calcd for $C_{19}H_{22}O_6N_4$ (402.4): C, 56.71; H, 5.51; N, 13.92; O, 23.85. Found: C, 56.58; H, 5.65; N, 13.95; O, 23.78.

Preparation of 1-[*N*-(4′-Nitro-1′-phenylazo-*p*-phenyl)-*N*-methylaminohexanoyl]glycerol (4b). Compound **4b** was prepared in the way described for **4a,** mp 135.4–136 °C. Anal. Calcd for $C_{22}H_{28}O_6N_4$ (444.3): C, 59.45; H, 6.30; N, 17.61; O, 21.62. Found: C, 59.40; H, 6.17; N, 17.72; O, 21.55.

Preparation of 1-[*N*-(4′-Nitro-4-biphenylazo-*p*-phenyl)-*N*-methylaminopropinoyl]glycerol (4c). 4′-Nitro-4-aminobiphenyl was azotized and coupled with **2a** as described for **4a,** mp 143.6–145.0 °C. Anal. Calcd for $C_{25}H_{26}N_4O_6$ (478.4): C, 62.76; H, 5.48; N, 11.71; O, 20.05. Found: C, 62.70; H, 5.37; N, 11.80; O, 20.01.

Preparation of 1-[*N*-(*p*-Formylphenyl)-*N*-methylaminopropionyl]glycerol (3a). The aldehyde **3a** was synthesized by the method described for *p*-dimethylaminobenzaldehyde.[12] $POCl_3$ (3 g, 20 mmol) was added dropwise with stirring to 20 mL of dimethylformamide while the mixture was cooled in an ice bath. After 30 min 5.5 g (19 mmol) of **2a** was added dropwise and stirring was continued for 1 day at room temperature. The mixture was then poured over crushed ice. The solution was neutralized to pH 6 by the dropwise addition of aqueous sodium acetate and decanted from a precipitated oil. Then neutralization was continued to pH 8 and the solution was stored in the refrigerator overnight. A pale brown oil precipitated which was the desired aldehyde (**3a**). By extracting the aqueous solution with dichloromethane the yield of the aldehyde **3a** was increased. The next reaction was performed without further purification of the product.

Preparation of 1-[*N*-(*p*-Formylphenyl)-*N*-methylaminohexanoyl]glycerol (3b). Compound **3b** was prepared in the way described for **3a.**

Preparation of 1-[*N*-(4′-Nitrostilben-4-yl)-*N*-methylaminopropionyl]glycerol (Trans Isomer) (5a).[13] The stilbene compound **5a** was synthesized by the Perkin condensation described in ref 10. A mixture of 10 mmol of the crude aldehyde **3a,** 12 mmol of *p*-nitrophenylacetic acid, and 10 drops of piperidine was heated to 140 °C for 1 h. A red cake remained after the mixture was cooled. The product was dissolved in hot acetic acid and water was added until the hot solution became turbid. After cooling, a red, viscous product precipitated which was filtered off and purified by column chromatography (silica gel, ethyl acetate/methanol, 1:5 v/v). The pure product was of rubber-like consistency. Anal. Calcd for **5a,** $C_{21}H_{24}N_2O_6$ (400.4): C, 62.99; H, 6.04; N, 6.99; O, 23.96. Found: C, 63.12; H, 6.12; N, 7.12; O, 23.85.

Preparation of 1-[*N*-(4′-Nitrostilben-4-yl)-*N*-methylaminohexanoyl]glycerol (Trans Isomer) (5b). Compound **5b** was prepared in the way described for **5a.** Anal. Calcd for **5b,** $C_{24}H_{30}N_2O_6$ (442.46): C, 65.15; H, 6.83; N, 6.33; O, 21.96. Found: C, 65.28; H, 6.75; N, 6.25; O, 22.10.

General Method for Preparation of the Diglyceride-Like Compounds III–IX. The diglycerides III–IX were synthesized by acetylating the chromophoric monoglycerides with fatty acid chlorides: 0.8 mmol of the monoglyceride and 1 mmol of pyridine were dissolved in 20 mL of anhydrous dioxane and cooled to 10 °C. The appropriate fatty acid chloride (1 mmol) was added dropwise with vigorous stirring over 15 min and the stirring continued for an additional 4 h. The dioxane was evaporated and the residue was extracted with ether, washed with 0.5 N citric acid to remove pyridine, and washed with 1 N $NaHCO_3$ and water. The organic phase was dried (Na_2SO_4) and evaporated. The residue was purified by column chromatography. Merck silica gel was used, particle size 0.06–0.2 mm, and a mixture of benzene/ethyl acetate, 3:1 v/v, as eluent. Three main fractions of dyes were separated with R_f values, obtained from thin layer chromatography, as follows: fraction 1, R_{f1} ~0.95; fraction 2, R_{f2} ~0.45, R_{f3} ~0.40; fraction 3, R_{f4} ~0.1. Elemental analyses confirmed that fraction 1 was the triglyceride (diacylated product), fraction 2 the desired diglyceride (monoacylated product), and fraction 3 the monoglyceride (nonacylated product). The pooled fraction 2 (R_f 0.45–0.40) was evaporated and the residue recrystallized from methanol (yield ~60%).

^1H NMR spectral data for dye VI: δ 0.89 t (3 H), 1.27 s (24 H), 1.61 br (2 H), 2.35 t (2 H), 2.43 d (1 H, exchanges with CH_3OD), 2.72

Table II. Elemental Analyses, Melting Points, and Mass Spectral Data of the Diglycerides III-IX

compd	formula	calcd (found), % C	H	O	mp, °C	MS m/e (M^+)
III	$C_{42}H_{66}N_4O_7$	68.30 (68.47)	8.94 (8.97)	15.18 (15.21)	79-81	738
IV	$C_{38}H_{58}N_4O_7$	66.86 (66.90)	8.50 (8.50)	16.45 (16.42)	81-82	682
V	$C_{39}H_{60}N_4O_7$	67.24 (67.00)	8.62 (8.60)	16.04 (16.09)	93.0-94.5	696
VI	$C_{35}H_{52}N_4O_7$	65.62 (65.44)	8.12 (8.05)	17.50 (17.72)	94-95	640
VII	$C_{42}H_{64}N_2O_7$	71.19 (71.00)	9.04 (9.00)	15.82 (15.91)	109-110	708
VIII	$C_{37}H_{54}N_2O_7$	69.65 (69.68)	8.53 (8.58)	17.54 (17.90)	100-102	638
IX	$C_{43}H_{60}N_4O_7$	69.33 (69.36)	8.05 (8.28)	15.03 (14.89)	136.5-138	745

Table III. Characteristic Monolayer Data for the Liquid-Expanded and the Condensed State of Dyes I-IX on $CdCl_2$ Subphase[a]

	limiting area[b]	first inflection point[c]		limiting area[b]	second inflection point[c]		area, Å², at
compd	$a_{\pi\to0}$, Å²	a_{T1}, Å²	π_{T1}, dyn/cm	$a_{\pi\to0}$, Å²	a_{T2}, Å²	π_{T2}, dyn/cm	π = 25 dyn/cm
I	118.0	114.0	1.0	50.0			45.0
II				51.0			46.0
III	112.0	93.5	6.0	21.5			20.5
IV	112.0	91.5	6.4	22.0			19.0
V	103.0	88.0	4.6	37.5	30.0	15.0	21.0
VI	101.0	87.0	5.0	34.0	29.0	22.0	20.0
VII	100.0	94.0	2.0	39.0			32.5
VIII	93.0	84.0	2.4	29.0			31.5
IX				34.0			31.5

[a] The data for the liquid-expanded state of dye I are obtained for NaCl subphase. [b] $a_{\pi\to0}$ ("area at zero pressure") is obtained by extrapolation of the steep linear part of the π-a isotherm to π = 0 dyn/cm. [c] The subscripts T1 and T2 are related to the first and second phase transition, respectively, which are indicated by an inflection of the isotherms.

t (2 H), 3.13 s (3 H), 3.74 t (0.35 H), 3.83 t (2 H), 4.05-4.30 m (4.5 H), 5.11 br (0.15 H), 6.79 d (2 H), 7.92 d (2 H), 7.94 d (2 H), 8.34 d (2 H). Dye VIII: δ 0.89 t (3 H), 1.26 s (24 H), 1.60 br (2 H), 2.34 t (2 H), 2.40 d (1 H, exchanges with CH_3OD), 2.66 t (2 H), 3.00 s (3 H), 3.66-3.80 m (2.35 H), 4.03-4.37 m (4.5 H), 5.11 br (0.15 H), 6.72 d (2 H), 7.07 q (2 H, J = 15.8 Hz), 7.44 d (2 H), 7.57 d (2 H), 8.19 d (2 H). As concluded from these data the chromophoric diglycerides consist of about 15% of 1,2-diglycerides and 85% of 1,3-diglycerides. The stilbene chromophores are pure trans isomers (vinylene protons: δ 7.07 q, coupling constant J = 15.8 Hz).

Spreading Solvent and Subphase. Chloroform was first washed with concentrated sulfuric acid and water, then distilled on $CaCl_2$, and finally passed over a basic aluminum oxide column. Doubly distilled water (once on alkaline permanganate, once on sulfuric acid) was used to prepare all aqueous solutions. The subphase contained 1 mM NaCl (Suprapur grade, Merck, Darmstadt) or 0.4 mm $CdCl_2$ (p.a. grade, Riedel de Haen, Seelze-Hannover). The pH of the salt solutions was kept at 6.7 by addition of $NaHCO_3$ (usually 0.05 mM). The pure water had a pH of about 5.8. The $CdCl_3$ subphase was chosen, because of its use for deposition of a monolayer on solid substrates.

Surface Pressure-Surface Area Measurements. Surface pressure-surface area isotherms (π-a isotherms) were determined using a circular trough of polypropylene and a Langmuir balance as previously described.[5] A 1 mM solution (0.0500 mL, Agla microsyringe) of the dyes in chloroform was spread on a 1000-cm² aqueous surface. π-a isotherms were generated at different compression rates. Usually the compression rate for the surface area interval 390-170 Å²/molecule was 50 Å² molecule^{-1} min^{-1} and for the remaining surface area 20-3 Å² molecule^{-1} min^{-1}. Very slow compression rates were achieved by intermittent compression and equilibration. Pressure-area measurements were commenced 4 min after addition of spreading solution. For all measurements the temperature was 20.5 ± 0.2 °C.

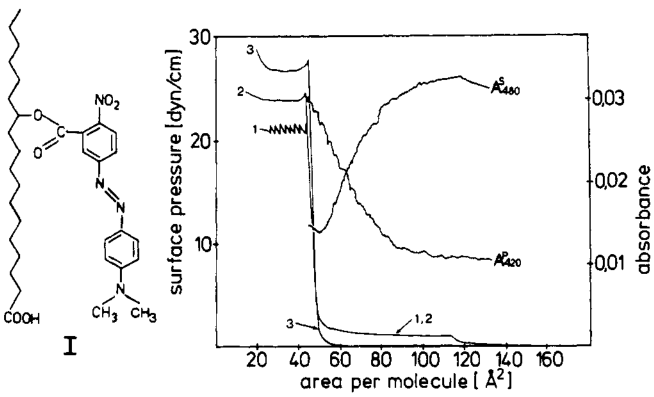
Spectroscopic Measurements. Surface absorption spectra, monolayer scanning records, and surface absorption-surface area isotherms were obtained using a single-beam, single-reflectance photometer. The photometer and the methods of measuring have been described by Fromherz.[14,15] The light beam was polarized by a Glan-Thomson prism and passed through a 45° prism to get an angle of incidence of 45°. The reflected intensities from the monolayer and from the mirror below the monolayer were measured by a photomultiplier. In this way it was possible to record linearily polarized absorption spectra of dye monolayers at the air-water interface. Spectra of dye solutions were measured using a Cary 14 spectrophotometer.

Symbols. π, surface pressure (dyn/cm); π_T, transition surface pressure; a, surface area per molecule (Å²/molecule); π-a curve, surface pressure vs. area per molecule plot; A, monolayer absorbance; λ, wavelength (nm); λ_{max}, wavelength of the absorbance maximum; A-λ curve, surface absorbance vs. wavelength plot; A-a curve, surface absorbance vs. surface area per molecule plot; subscripts to letter A, wavelength (nm); superscripts to letter A, s:s-polarized light (electric vector of the light is normal to the plane of incidence); p:p-polarized light (electric vector of the light is in the plane of incidence); $D = A^s/A^p$, dichroic ratio.

Results

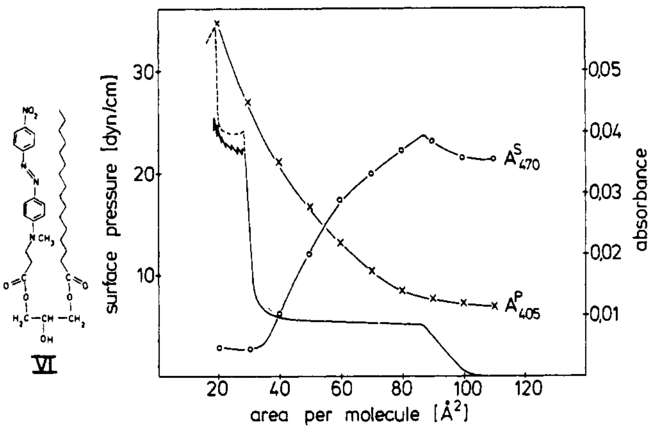
Surface Pressure-Surface Area Isotherms. 1. Chromophoric Stearic Acid Derivatives (Dyes I and II). Characteristic areas and surface pressures are summarized in Table III. π-a isotherms are given in Figure 1 for I on pure water and on NaCl and $CdCl_2$ subphases. The π-a isotherms on pure water and on the NaCl subphase exhibit an inflection at 114 Å²/molecule and 1 dyn/cm. From this point the surface pressure remains nearly constant up to an area of approximately 50 Å²/molecule and then increases rapidly until the film collapses. Beyond the point of collapse the surface area of the monolayer on pure water is decreased by 2 Å²/molecule and then kept constant for 2 min. The surface pressure increases during compression and decreases during equilibration (Figure 1, curve 1, $\Delta\pi \simeq$ 1 dyn/cm). After an equilibration time of 2-3 min the surface pressure attains a constant value. In comparison, the postcollapse π for the monolayer of dye I on the NaCl subphase remains constant during compression and equilibration. Cd^{2+} ions have a strong effect on the shape of the π-a isotherm (Figure 1, curve 3): a plateau region for areas between 50 Å²/molecule and of the condensed film decrease. Repeated compression of the monolayer of I on pure water-NaCl and -$CdCl_2$ subphases to 25 Å²/molecule and subsequent expansion to 140 Å²/molecule has no essential effect on the shape of the π-a isotherm. The π-a isotherms of dye II for different subphases are similar to that of dye I on $CdCl_2$ subphase up to a surface pressure of about 25 dyn/cm. The monolayer II collapses at an area of about 40 Å²/molecule, forming small dye crystals. The collapse pressure, which depends on compression rate, is in the range of 40-45 dyn/cm.

2. Chromophoric Diglyceride Derivatives (Dyes III-IX). Here, only π-a isotherms of dyes III, VI, VIII, and IX are illustrated because they show the representative details of mo-



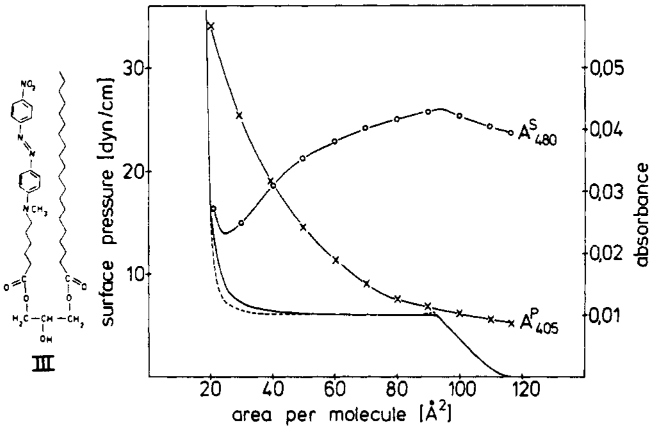
I

Figure 1. Surface pressure-area and surface absorbance-area plots for I. Curve 1, pure water, pH 5.8; curve 2, 1.0 mM NaCl, pH 6.8; curve 3, 0.5 mM $CdCl_2$, pH 6.8; A^{s}_{470}-a curve and A^{p}_{420}-a curve, 1.0 mM NaCl, pH 6.8. The zigzag curve in the range of 45-20 Å^2/molecule is obtained by intermittent compression and equilibration (equilibration time < 2 min).



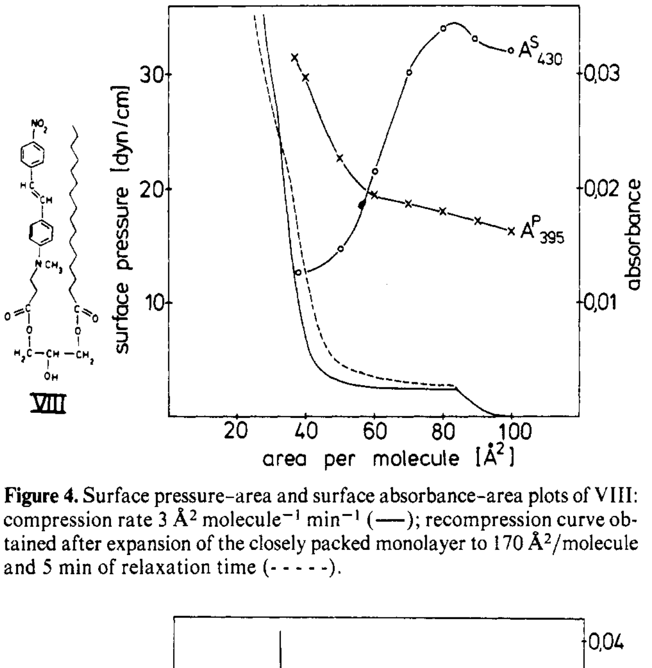
VI

Figure 3. Surface pressure-area and surface absorbance-area plots for VI: compression rate 3 Å^2 molecule^{-1} min^{-1} (——), the zigzag curve between 30 and 20 Å^2/molecule is obtained by intermittent compression and equilibration (equilibration time < 4 min). Compression rate 15 Å^2 molecule^{-1} min^{-1} (- - - - -).



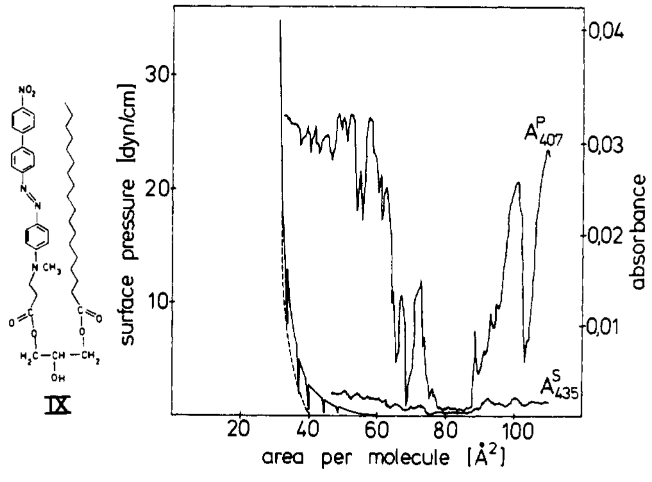
III

Figure 2. Surface pressure-area and surface absorbance-area plots for III: Compression rate 5 Å^2 molecule^{-1} min^{-1} (——); compression rate 15 Å^2 molecule^{-1} min^{-1} (- - - - -).



VIII

Figure 4. Surface pressure-area and surface absorbance-area plots of VIII: compression rate 3 Å^2 molecule^{-1} min^{-1} (——); recompression curve obtained after expansion of the closely packed monolayer to 170 Å^2/molecule and 5 min of relaxation time (- - - - -).



IX

Figure 5. Surface pressure-area and surface absorbance-area plots of IX: compression rate 5 Å^2 molecule^{-1} min^{-1}, between a = 50 and 33 Å^2/molecule intermittent compression and equilibration (——); recompression curve (- - - - -).

nolayer behavior of diglyceride-like dyes. As subphase we chose an aqueous $CdCl_2$ solution because of its use for built-up films in our laboratory. No essential changes in the shape of the isotherms were observed when these surfactants were spread on distilled water. Characteristic areas and the corresponding surface pressures are summarized in Table III.

The π-a isotherms of those compounds which consist of two aromatic rings (compounds III-VIII) exhibit a transition from a liquid-expanded through an intermediate to a condensed state (see Figures 2-4), for which we use the term "first transition region" in the following discussion (about monolayer states and phase transformation, see ref 16). It is interesting to note that the first transition pressure (π_{T1}) for the azo dyes III-VI is much higher than for the stilbene dyes VII and VIII. After passing the first transition region the π-a curve of III and V turns upward at an area of 22 Å^2/molecule while those of IV and VI-VIII rise steeply at 35-40 Å^2/molecule. At further compression the azo compounds IV and VI pass through a second transition until an area of about 20 Å^2/molecule is approached and the surface pressure increases steeply again. In contrast to the two-membered-ring compounds III-VIII the three-membered-ring compound IX shows no abrupt phase transition, but it may be assumed that a gradual structural change between 60 and 40 Å^2/molecule occurs, as indicated by the form of the π-a curve in Figure 5, which is obtained by intermittent compression and equilibration (equilibration time about 2 min).

In order to investigate whether the observed phase transformations are related to irreversible structural changes of the monolayers, recompression experiments were performed. The azo compounds III-VI were at once compressed to an area of 22 Å^2/molecule, then expanded to about 180 Å^2/molecule and immediately recompressed. The recompression curves show

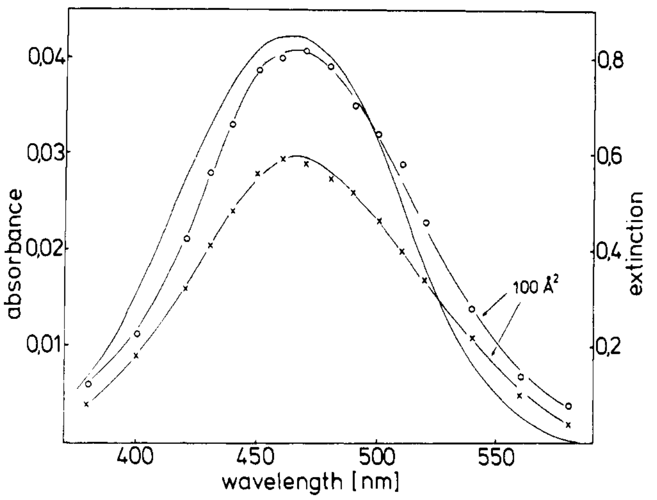


Figure 6. Absorbance spectra of VI: ethanol solution, c 2.5 × 10^{-5} mol/L, λ_{max} 465 nm (—). Monolayer on aqueous subphase, a = 100 Å²/molecule, s-polarized light (o-o-o); p-polarized light (x-x-x); λ_{max} 470 nm.

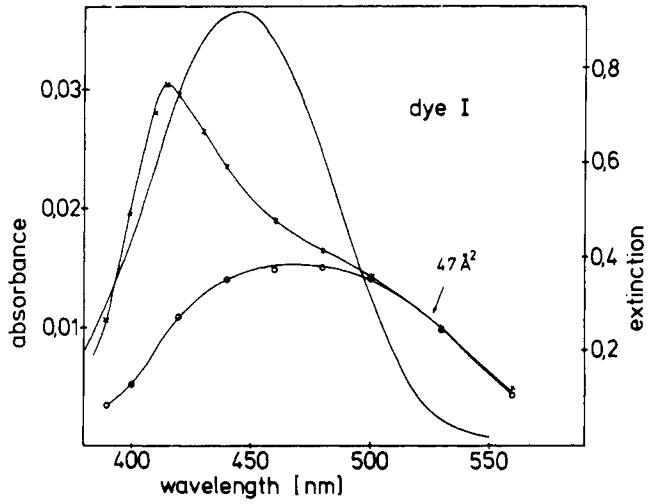


Figure 7. Absorbance spectra of I: cyclohexane solution, c 3.1 × 10^{-5} M, λ_{max} 443 nm (—); monolayer on pure water a = 47 Å², s-polarized light (o-o-o); p-polarized light (x-x-x).

no essential changes when compared with the first compression curves. The recompression curve of IX is nearly identical with the curve obtained by intermittent compression (for IX see Figure 5, dotted line). The complete reversibility of the π-a isotherms observed with the azo compounds III-VI cannot be found with the stilbene compounds VII and VIII. In Figure 4 the recompression curve of VIII is only identical up to the first transition pressure. The extrapolated "area at zero pressure" for the condensed state of the recompression curve increases by 8 Å²/molecule when compared with that of the first compression, indicating irreversible structural changes of the monolayer.

Absorbance Measurements. Under the condition that the water surface is covered by a coherent monolayer which is indicated by an initial rise of the π-a curve, reproducible monolayer absorbance spectra are easily obtained by moving the enclosed films at constant area into the light beam of the monolayer photometer (absorbance signal) and out of it (reference signal). The obtained linearly polarized spectra give information about the state of aggregation and the state of orientation of the chromophoric surfactants. In Figure 6 the polarized absorbance spectra for monolayer VI at a = 100 Å²/molecule and the corresponding solution spectrum are depicted. These spectra are typical for monolayers of I and III-VIII in the liquid-expanded state. The s- and p-polarized spectra are very similar to those in polar solution. The dichroic ratios calculated for the maxima of the polarized bands are in the range of D = 1.4-1.35. As shown in the Appendix the expected value of the dichroic ratio in the case of statistical orientation of the π-π^* transition moments in the layer plane is 1.40.

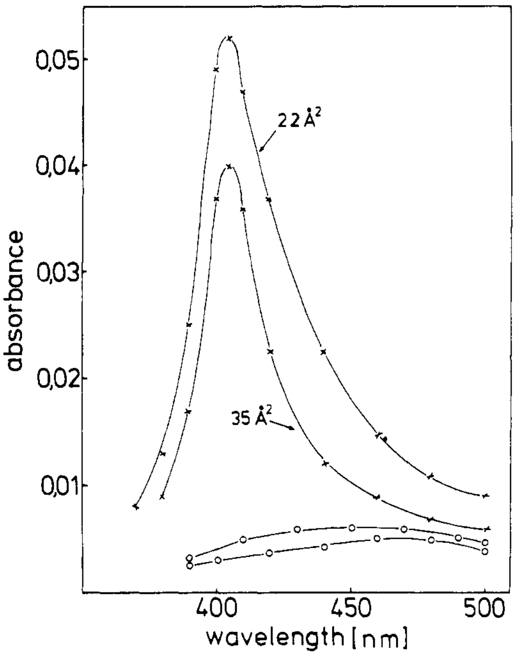


Figure 8. Absorbance spectra of monolayer VI on aqueous subphase for two different surface areas: first condensed state at a = 35 Å²/molecule; second condensed state at a = 22 Å²/molecule; s-polarized light (o-o-o); p-polarized light, λ_{max} 405 nm (x-x-x).

The π-a curve of II and IX does not suggest a coherent, liquid-expanded monolayer at areas of about 100 Å²/molecule. Reproducible surface absorbance spectra could not be obtained at a >60 Å²/molecule, because of strong absorbance fluctuations (see Figure 5, also section "Surface Absorbance-Surface Area Isotherms").

The Condensed State. Polarized surface absorbance spectra of condensed films are measured at surface areas which are given by the initial steep rise of the π-a curves. The spectra illustrated in Figures 7-10 show two characteristic features.

1. A narrow and strong band appears in each p-polarized spectrum. The position of the absorbance maximum is shifted 30-50 nm to shorter wavelengths when compared to the corresponding dye spectra in polar solvents (e.g., $CHCl_3$). This hypsochromic shift cannot be explained by a "solvatochromic effect", because, for example, the position of the absorbance maximum of VI shifts only from 465 nm in ethanol to 440 nm in cyclohexane. In comparison, the main peak of the p-polarized spectrum of the condensed monolayer of VI shifts from 465 nm in the liquid-expanded state (Figure 6) to 405 nm in the condensed state (Figure 8). These facts make it reasonable to suppose that the narrow bands which appear predominantly in the p-polarized spectra must be attributed to arrangements of the chromophores in a pincushion planar lattice, the dipole moments and the transition dipoles for the absorption band under study being oriented normal to the plane (so-called H aggregates). Since the interaction of the transition dipoles is repulsive a blue shift of the absorption band for H aggregates (H band) compared with monomer band occurs.[17,18]

2. At the long-wavelength side the shape of the s-polarized spectra is similar to those which are obtained for liquid-expanded states and for dyes in polar solvents. Therefore we assign these broad bands to a population of monomeric species

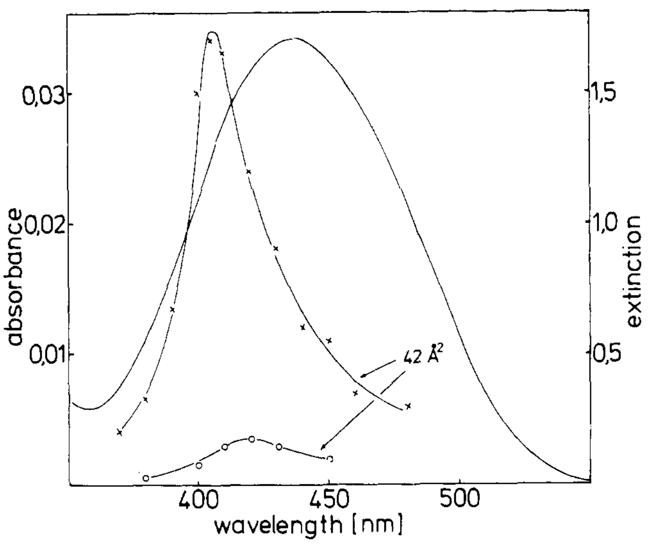


Figure 9. Absorbance spectra of IX: chloroform solution (+ 1% ethanol), c 4.5 × 10^{-5} mol/L, λ_{max} 435 nm (—). Condensed monolayer on aqueous subphase, a = 42 Å^2/molecule; s-polarized light, λ_{max} 420 nm (o-o-o); p-polarized light, λ_{max} 405 nm (x-x-x).

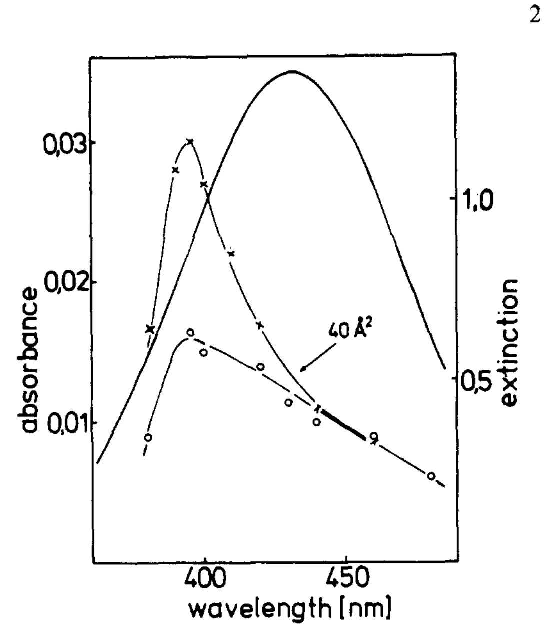


Figure 10. Absorbance spectra of VIII: chloroform solution (+ 1% ethanol), c 4.8 × 10^{-5} mol/L, λ_{max} 432 nm (—). Condensed monolayer VIII on aqueous subphase, a = 40 Å^2/molecule; s-polarized light (o-o-o); p-polarized light λ_{max} 395 nm (x-x-x).

in the condensed films (M band). A M band appears also as a shoulder in the p-polarized spectra of dyes I, III-V, VII, and VIII. The polarized absorbance spectra of dye I (Figure 7) is similar to those observed for the azo derivatives III-V. These condensed films are supposed to consist of H aggregates and isotropically distributed monomers. The condensed monolayers of the azo dyes VI and IX, however, consist exclusively of H aggregates, as indicated by their strong dichroism (see Figures 8 and 9). As typical spectra of condensed stilbene films of II and VII-VIII we depicted that of dye VIII (Figure 10). The s-polarized and the p-polarized spectra exhibit an aggregate band at short wavelength whose dichroic ratio is 0.5. At longer wavelength the A^p-λ curve changes into the A^s-λ curve and tails to the red. A most reasonable explanation of this is that the condensed film consists of aggregates with transition dipoles tilted to the layer plane and of monomers whose transition dipoles are statistically distributed.

Surface Absorbance (*A*)-Surface Area (*a*) Isotherms. Information about changes of molecular aggregation and orientation caused by compression of the monolayer can be derived from A-a isotherms. The absorbances at λ_{max} of the M band for s-polarized light and at λ_{max} of the H band for p-polarized light are continually measured as a function of the surface area (Figures 1-5). The compression rate is 20 Å^2 molecule^{-1} min,$^{-1}$ which is the lowest limit of the double-barrier trough used in the spectroscopic device.

The A^s-a and A^p-a curves of the compounds I and III-VIII show a similar feature between areas of 110 and 40 Å^2/molecule. The A^p-a curves increase slightly when going from 110 to 60-80 Å^2/molecule and rise steeply up to the limiting areas of the condensed states. The A^s-a curves increase linearly at once to areas which correspond to the first inflection point of the π-a curves and then decrease parabolically. From these facts we conclude that H aggregates are formed only when the molecular surface density exceeds the value of about 14 × 10^{14} molecules/cm^2 (adequate to a = 70 Å^2/molecule), while the surface density of the flat-lying monomeric species decreases as soon as the films change to the first intermediate state. In case of film IX the measured absorbance A^p_{407} oscillates between 0.03 absorbance unit at a > 65 Å^2/molecule (Figure 5). With decreasing surface area the absorbance fluctuations decrease and the shape of the A^p-a curve changes to an ascending line when the film becomes coherent. The A^s-a curve was measured at λ 435 nm, which is the expected λ_{max} of the M band (solution spectrum, λ_{max} 435 nm, Figure 9). Only weak oscillations of the absorbance close to the zero line are recorded. These results demonstrate that at surface areas between 60 and 110 Å^2/molecule the monolayer of IX does not change from the liquid-expanded state (chromophores are lying flat on the water surface) to the condensed state (H aggregates) but forms islands of H aggregates immediately after spreading. A similar behavior was observed for dye II and for dye I on $CdCl_2$ subphase.

Monolayer Scanning. In order to obtain information about the monolayer state at large areas (a > 250 Å^2/molecule) where no surface pressure is measurable, monolayer scanning experiments are performed. As a typical example, monolayer scanning records of VI are depicted in Figure 11. The absorbance is measured at 470 nm with s-polarized light, because at high surface areas only the M band is expected. At a film area of 330 Å^2/molecule fluctuations between 0 and 0.04 absorbance unit are observed which decrease to 0.02 at a = 170 Å^2/molecule. This means that at high areas the film molecules do not separate completely from one another, but form small clusters or islands. Considering the width of the fluctuation peaks the diameters of the film islands are found to be 1-10 mm. Absorbance fluctuations vanish at film areas which coincide with those corresponding to the first rise of π-a curves.

Discussion

π-a isotherms are usually interpreted by means of molecular CPK models. The area which is occupied by the surfactant in the monolayer (obtained from π-a isotherms) is simulated by the cross-sectional area of a certain conformation of an adequate molecular CPK model and from this the arrangement of the molecules in the monolayer is inferred. Playing with CPK models one has to consider the multipolar amphipathic properties of the surfactants. For the dye molecules I-IX we have to assume several hydrophilic centers such as carboxylic, ester, azo (-N=N-), and amino groups, which have an affinity to the water surface. Besides these water-chromophore interactions we anticipate that interactions between the paraffin chains and between the aromatic rings of the chromophores (chain-chain interaction, chain-ring interaction, and ring-ring interaction) have an important influence on the monolayer properties, especially in case of close-packed condensed films.

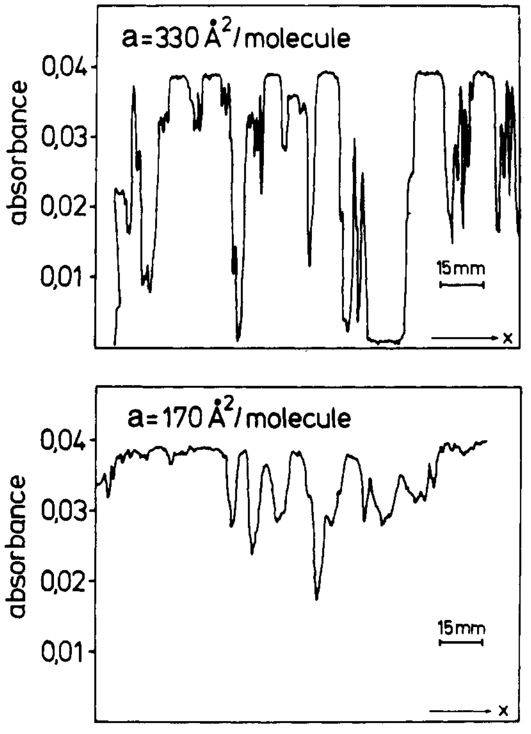


Figure 11. Absorbance-scanning records of monolayer VI: during film movement at constant area through the light beam (in direction of the x axis) the absorbance at 465 nm (absorption maximum of the M band) is recorded.

We shall follow this concept and compare its conclusions with the spectroscopic findings.

At surface areas where the first rise of pressure is detectable the monolayers become coherent. The corresponding areas for dyes I (NaCl subphase) and III-VIII agree well with the edge-on conformation of the flat-lying molecular CPK model (see schematic drawings in Figure 12A,B). This conclusion is also consistent with that drawn from the polarized absorption spectra (Figure 6, $D = 1.4$). The first transition pressure, π_{T1}, indicates the change of orientation of the chromophores. Therefore it is plausible to assume that the magnitude of this "lifting-off pressure" reflects the strength of hydrophilic affinity of the chromophores. For the azo dyes III-VI π_{T1} is in the range of 4.6-6.4 dyn/cm, whereas for the corresponding stilbene dyes VII and VIII π_{T1} is in the range of 2.0-2.4 dyn/cm. The most reasonable explanation for this is that the azo group (-N=N-) adheres much more strongly to the water surface than the vinylene group (-CH=CH-) (in the stilbene dyes only the azo group is substituted by the vinylene group). A further decrease of hydrophilic affinity of chromophores is observed in case of linkage of the chromophore via the ester bond to 12-hydroxystearic acid (dyes I and II) or by an increase of length of the chromophore (dye IX consists of three aromatic rings). For dye I (NaCl subphase, or distilled water) a surface pressure of 1 dyn/cm is enough to detach the chromophore from the water surface. In case of dye II and the three-ring chromophore of dye IX the hydrophilic affinity of chromophores is assumed to be not strong enough to stabilize a flat-lying edge-on conformation. As shown by the π-a isotherms and spectroscopic results these dyes form close-packed condensed films immediately after spreading. A similar behavior is observed for dye I spread on $CdCl_2$ subphase. Here, the interaction between Cd ions and the carboxylic groups causes a close-packed film compensating the hydrophilic interaction energy of the chromophores.

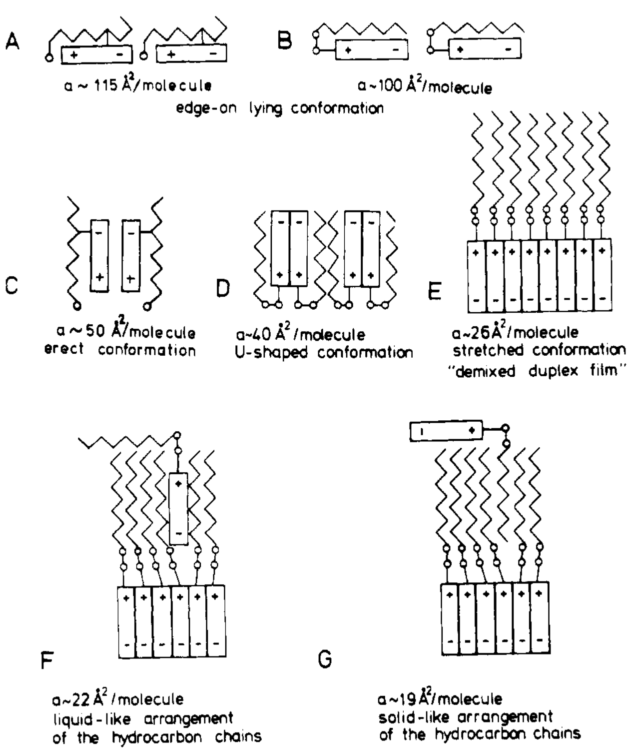


Figure 12. Schematic drawing of various geometrical arrangements of the chromophoric surfactants for different monolayer states. The chromophores are represented by rectangles with indication of their static dipoles. Zigzag lines: paraffin chains. The indicated molecular areas are obtained from corresponding CPK molecular models. In cases F and G, respectively, the areas correspond to monolayers where a portion of 15 and 25% of the molecules is squeezed into the upper part of the layer, respectively (for details see Discussion).

In the condensed state dyes I and II occupy an area of about 50 Å^2/molecule, which is consistent with the cross-sectional area of a molecular CPK model in the erect conformation (see Figure 12C). The polarized absorption spectra of dye I (Figure 7), however, show that we have to assume a heterogeneous arrangement in which about 50% of the molecules form H aggregates and the other 50% are monomers, whose transition dipoles are statistically distributed. In case of dye II the dichroism ($D = 0.85$ for λ_{max} 415 nm) indicates that the predominant portion of the chromophores is tilted to the surface plane.

In the case of the diglyceride-like dyes III-IX a chromophoric molecule and a fatty acid are chemically joined via an ester bond to one molecule of glycerol. Two simple molecular conformations are conceivable for these molecules in the condensed monolayer: the U-shaped conformation with $a \simeq 45$ Å^2/molecule and the stretched conformation with $a \simeq 26$ Å^2/molecule, respectively (Figures 12D and 12E, respectively).

The limiting areas, however, found for the condensed states of III-IX are consistent with neither of them. Further, we expect for both conformations a strong absorbance for p-polarized light and practically no absorbance for s-polarized light. But this is only found for dyes VI and IX. Taking into account that (1) molecules with paraffin chains of 20 carbon atoms (dyes III and V) have a greater tendency (stronger chain-chain attraction) to enter and remain in the closest packed arrangement than molecules with palmitoyl residues (16 carbon atoms, dyes IV and VI), (2) water molecules which interact with the polar glycerol group counteract chain-chain attraction, and (3) the cross-sectional area of the paraffin chain is about 7 Å^2 smaller than that of the chromophore, we may find models for the molecular arrangement of the condensed states which agree well with the experimental findings. In case of dyes III and V we observe the condensed state at about 20 Å^2/molecule and the collapse pressure does not occur below 40 dyn/cm. This behavior shows that strong attractive forces between the hydrocarbon chains predominate and force the molecules into the stretched conformation with dehydrated glycerol groups. As the cross-sectional area of the chromophoric portion is a bit larger than that of a paraffin chain, we suppose that a closest packed arrangement of the paraffin chains is realized by squeezing out a part of 25% of the chromophoric portions of the molecules as it is schematically illustrated in Figure 12G. This molecular arrangement is also supported by the polarized absorbance spectra, which exhibit a dichroic H band and a nonpolarized M band (e.g., for dye III: $D = 0.46$ for$\lambda_{\max}$ 413 nm and $D = 1$ for λ 480 nm).

For the first condensed state of dyes IV and VI we assume that the molecules (stretched conformation) are organized to two-dimensional bi- or multimolecular associates with palmitoyl residues randomly intertwined and vertically aligned chromophores (phase transitions of monoglycerides are interpreted in a similar way[20]). The area of 35 Å^2/molecule may be related to bulky hydrated glycerol groups. To account for the polarized spectra, monolayer VI is assumed to consist of small H aggregates, whereas monolayer IV consists of H aggregates which are surrounded by randomly oriented monomers. On further compression the glycerol groups become dehydrated, which leads to molecular rearrangement as reflected by the second plateau region of the π-a curve and the polarized spectra. In case of dye VI we observe at 22 Å^2/molecule a broadening of the p-polarized band relative to that of the first condensed state, which is assigned to a small fraction of monomers and dimers beside H aggregates, whose transition dipoles are normal to the layer plane (Figure 8). In good agreement with these results we find a model for the molecular arrangement according to Figure 12F, where a part of 15% of the dye molecules are supposed to be squeezed into the hydrocarbon layer filling the gaps between the palmitoyl residues. For the second condensed state of IV it is impossible to suppose a simple model for the molecular arrangement which is consistent with the polarized spectra and the assumptions made above. The π-a curves of compounds VII-IX show that at approximately 40 Å^2/molecule the monolayers are condensed and resist further compression. From this and the high dichroism of the polarized bands we conclude that the molecules are predominantly arranged in the U-shaped conformation according to Figure 12D, although it is not clear why the occupied area per molecule is a little bit smaller than that which is expected for the U-shaped molecule ($a \simeq 45$ Å^2/molecule).

The author knows that the supposed molecular arrangements of the condensed films are a little speculative, but the contribution of π-a isotherms and spectroscopic measurements in connection with molecular models can be considered as the first step to the understanding of the molecular structure of monolayers.

Acknowledgments. The author wishes to thank Professor H. Kuhn for encouragement and helpful discussions, Dr. P. Fromherz for provision of the photometer device, Mr. H. Meyer for advice in electronic problems, and Mrs. I. Reuber for help in preparing the dyes.

Appendix (see Figure 13)

Light Reflection and Refraction of a Very Thin Film at the Air-Water Interface. The generalized Fresnel formula for the reflection and refraction of light at a thin film can be simplified by linear expansion of the exponentials if $2\pi d/\lambda \ll 1$ (d = thickness of the film).[19] Under this condition the layer will be called a very thin film. A monomolecular anisotropic absorbing film can be characterized by three complex indexes of refraction, $\hat{n}_j = n_j - ik_j$, j: x, y, z; n_j real part of the refractive index; k_j absorption coefficient; $i = \sqrt{-1}$. For a first approximation we will assume $n_x = n_y = n_z = n_2$. If the π-π^* transition moment of the chromophores is randomly oriented parallel to the water surface, then $k_x = k_y$, $k_z = 0$ and Schopper's formula of reflection and refraction of very thin absorbing films is reduced (all terms second order in thickness d are neglected).

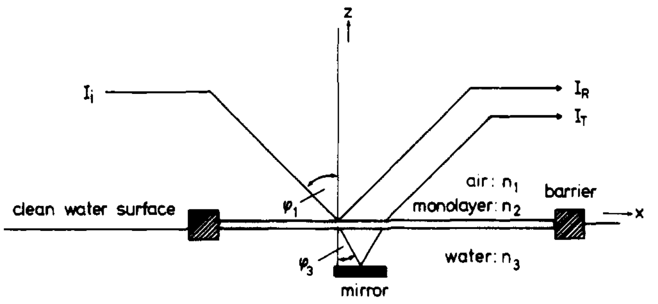


Figure 13. Diagram of the single beam monolayer photometer. I_i, I_R, and I_T are the incidental, the reflected, and the transmitted light intensities, respectively.

s Polarization

$$I_R{}^s = \frac{(n_3 \cos\phi_3 - n_1 \cos\phi_1)^2 + 4n_2k_x\eta(n_3\cos\phi_3 - n_1\cos\phi_1)}{(n_3\cos\phi_3 + n_1\cos\phi_1)^2 + 4n_2k_x\eta(n_3\cos\phi_3 - n_1\cos\phi_1)} \tag{1}$$

$$I_T{}^s = \left[\frac{4n_3\cos\phi_3\, n_1\cos\phi_1}{(n_3\cos\phi_3 + n_1\cos\phi_1)^2 + 4n_2k_x\eta(n_3\cos\phi_3 + n_1\cos\phi_1)}\right]^2 \tag{2}$$

$$\eta = 2\pi d/\lambda$$

p Polarization. $I_R{}^p$ and $I_T{}^p$ are obtained, when $n_1 \cos\phi_1$ and $n_3\cos\phi_3$ in eq 1 and 2 are replaced by $n_1/\cos\phi_1$ and $n_3/\cos\phi_3$, respectively. As reference signal, the reflectance I_{R0} and the transmittance I_{T0} of the pure water surface are measured. If $k_x = k_y = 0$, the above equations lead to the expressions for I_{R0} and I_{T0}. The measured absorbance of the monomolecular film is defined as

$$A = 1 - \frac{I_R + I_T}{I_{R0} + I_{T0}}$$

For monomolecular dye films the expression $4n_2k_x\eta$ is in the order of 0.06 ± 0.03. Inserting this value and $\phi_1 = 45°$, $n_3 = 1.333$, we obtain for the dichroic ratio $A^s/A^p = 1.40$.

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Studies on Monolayers. 2. Designed Monolayer Assemblies of Mixed Films of Surface-Active Azo Dyes

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Abstract: This paper is concerned with designed self-organization of surfactants to highly organized monomolecular layers, which may be used for molecular engineering. For this purpose the monolayer properties of two-component and three-component films are studied at the air-water and air-glass interface. The two-component films consist of the chromophoric diglyceride (VI) and the chromophoric triglyceride (X) (one fatty acid residue was substituted by *N*-(4′-nitro-1′-phenylazo-*p*-phenyl)-*N*-methylaminopropionic acid). The π–a curves of the mixed films showed marked deviations from the additivity rule. For the mole fraction 0.35 of the diglyceride component the surface pressure–area isotherm shows the characteristics of an "eutectic" film. The results of absorbance spectra and surface pressure–area isotherms suggest that the close-packed monolayer of the "eutectic" mixture consists of molecules in the stretched conformation with the chromophores in a card-pack-like arrangement (H aggregates). The three-component films consist of stearic acid, stearylamine, and 12-(4′-nitro-4-dimethylaminoazobenzene-3′-carbonyloxy)stearic acid (dye I). Complete miscibility of the three components in the film is observed for "neutral films", which are defined as a mixture whose molar ratio of total acid (stearic acid and dye I) and base (stearylamine) is 1:1. Neutral three-component films are deposited onto glass slides and absorbance spectra are measured with polarized light. The obtained absorption bands are approximated by two different Gaussian curves. From the analysis of the spectra it is concluded that in the deposited films dye monomers are in equilibrium with dye dimers; the association constant is calculated as 2.2×10^{-14} cm^2/dye molecule.

Introduction

Organized monolayer assemblies are of fundamental importance in biological systems. Recently they have also become interesting for molecular engineering, e.g., construction of photoelectric devices[1,2] or thin-film wave guides in integrated optics.[3] The starting point of constructing designed monolayer assemblies is the synthesis of surface-active molecules in a planned way, followed by the study of the behavior of these surfactants at the air-water interface. This was done in part 1 of this series,[4] where we have reported on pure monolayers of several new surface-active dyes whose properties and molecular architecture were studied by spectroscopic techniques and surface pressure–surface area measurements.

Often one-component monolayers cannot be transferred onto solid substrates, because the molecules do not form a closely packed and stable film. We suggest that this behavior may be caused by an unfavorable geometry of the molecules (the molecules do not interlock optimally) or repulsive intermolecular interactions (e.g., ion–ion interaction). In order to obtain stable monolayers of a high degree of order, other molecules are added which occupy the vacancy between the molecules or reduce the repulsion of the head groups. The present paper is concerned with two-component films whose monolayer behavior depends mainly on the geometry of the molecules and with three-component films, whose properties are strongly associated with the ion–ion interaction of the head groups.

Experimental Section

Materials. The syntheses of dyes I, VI, and X and the chemical data of I and VI are described in ref 4. Chemical data of X: mp 99.0–100.2 °C. Anal. Calcd for $C_{51}H_{82}O_8N_4$ (878.4): C, 69.70; H, 9.33; O, 14.57. Found: C, 69.81; H, 9.29; O, 14.31. Mass spectrum: m/e 878 (M$^+$). ^{1}H NMR ($CDCl_3$): δ 0.89 t (6 H), 1.26 s (48 H), 1.53–1.66 br (4 H), 2.31 t (4 H), 2.68 t (2 H), 3.11 s (3 H), 3.81 t (2 H), 4.10–4.39 m (4 H), 5.29 br (1 H), 6.79 d (2 H), 7.92 d (2 H), 7.94 d (2 H), 8.34 d (2 H).

Arachidic acid, stearic acid (STOOH), and stearylamine ($STNH_2$) (p.a. grade from E. Merck, Darmstadt) were twice recrystallized from ethanol. The chloroform (spreading solvent) and the doubly distilled water (subphase) were prepared as described in ref 4. The salts of $CdCl_2$, $NaHCO_3$ (p.a. grade), and KCl (suprapur grade) were purchased from E. Merck, Darmstadt.

Surface Pressure (π)–Surface Area (a) Measurements. The method is described in ref 1 and 4.

Preparation of Supports. As supports we used clean microscope glass slides (hydrophilic surface) and glass slides which were treated with $Si(CH_3)_2Cl_2$ (hydrophobic surface). The details of cleaning and preparations of the different supports are described in ref 1.

Film Deposition. For film deposition we used a rectangular trough ($18 \times 60 \times 0.6$ cm) of Teflon provided with a hollow for dipping the supports in and out of the monolayer-covered water surface. The trough was covered with a dust cover and placed on an antivibration table. A modified Langmuir-Blodgett technique[1] was used to transfer the monolayer to the glass support. A motor drive raised the plate slowly (0.5–2.0 cm/min) through the water-air interface, and a variable-speed motor drive moved the compressing barrier in such a way that the surface pressure remained constant during the deposition (surface pressure fluctuation <0.4 dyn/cm). The surface pressure was measured by a Wilhelmy balance. In order to control the quality of the spread films and the transfer ratio (ratio between the area of the deposited film and the corresponding geometrical area of the solid support) the surface pressure and the surface area were continuously recorded by a x–y recorder during film compression and deposition. The aqueous subphase contains $CdCl_2$ (4.5 mM) and $NaHCO_3$ (0.4 mM), pH 6.7.

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