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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 × 60 × 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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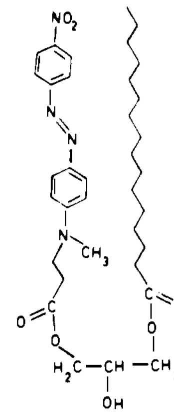

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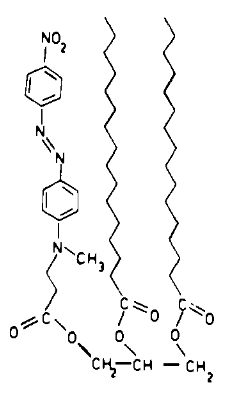

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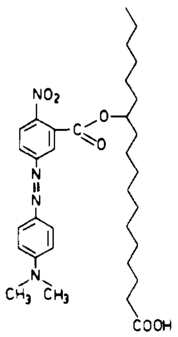

I

STOOH

STNH₂

Spectroscopic Measurements. Polarized absorption spectra of monolayers at the air-water interface were determined with a single-beam, single-reflectance photometer as previously described.[4-6] The transmission of linearly polarized light at an angle of incidence of 45° of dye monolayers and multilayers deposited on microscope slides was measured with the vibrating plate device.[1]

For symbols and definitions used in this text see ref 4.

Results

1. Mixed Monolayers Which Contain Dyes VI and X. Surface Pressure-Surface Area Isotherms. The π-a isotherms of monolayers of a series of mixtures at different composition ranging from the mole fraction of VI, $N_{\mathrm{VI}} = 1$, to the mole fraction of X, $N_{\mathrm{X}} = 1$, are shown in Figures 1 and 2. The subphase is doubly distilled water without buffer (pH 5.8, t = 22-23 °C). The compression rates are 50 Å^2 molecule^{-1} min^{-1} up to a surface area of 160 Å^2/molecule and 10 Å^2 molecule^{-1} min^{-1} for the remaining surface. At surface areas below 100 Å^2/molecule the compression is stopped at 10 Å^2/molecule intervals for 1-2 min to test film stability and to allow the monolayer to reach the equilibrium state. Cd ions or K ions have no pronounced effect on the π-a isotherms.

The π-a curves show van der Waals-like behavior with a first linear rise of surface pressure at areas between 100 and 115 Å^2/molecule. In the high-pressure region the isotherms of the pure and mixed films experience modifications which may be referred to structural changes exclusive of that of N_{VI} = 0.35, which rises steeply and linearly. The dotted lines of the π-a plots demonstrate that the monolayers are not stable in this region. As criteria for stability we define an upper limit of surface pressure drop of 1.0 dyn cm^{-1} min^{-1} at constant area. Following this definition, only the mixed monolayer of N_{VI} = 0.35 is stable even at surface pressures of 30-40 dyn/cm (see Figure 2).

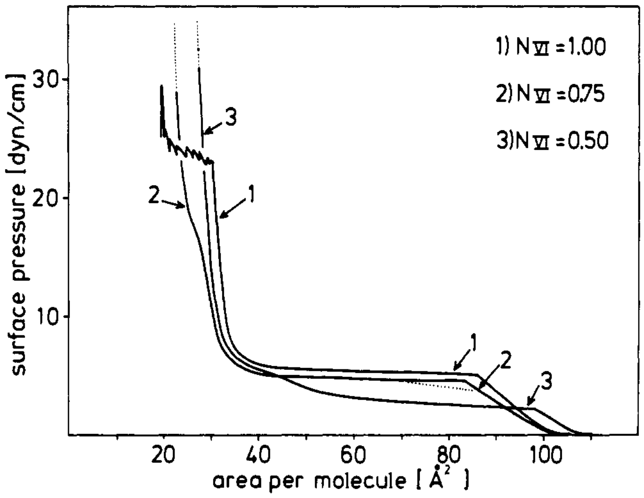

Figure 1. Surface pressure-area plots of dye VI and X mixtures on doubly distilled water, pH 5.8; t = 22-23 °C. Compression rate 10 Å^2 molecule^{-1} min^{-1} (——). The dotted part of curve 2 is obtained when film compression is stopped for 2 min (for details see text). Abscissa: average molecular area.

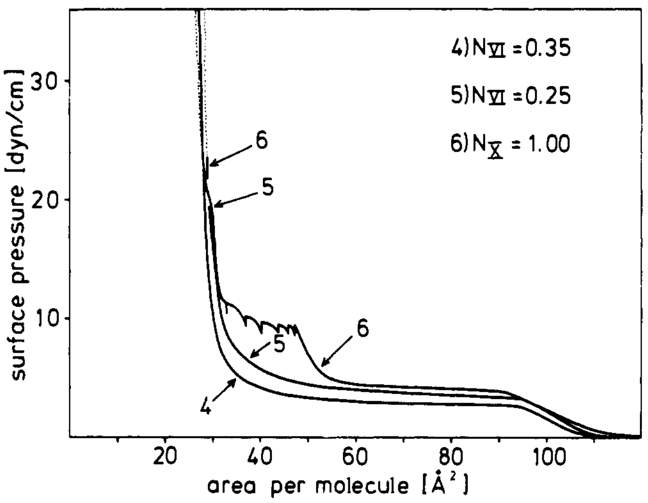

Figure 2. Surface pressure-area plots of dye VI and X mixtures on doubly distilled water, pH 5.8; t = 22-23 °C. Compression rate 10 Å^2 molecule^{-1} min^{-1} (——). Abscissa: average molecular area.

From theory of mixed films it has become customary to call monolayer-forming components immiscible if the mixed film obeys the "additivity rule", according to the equation

$$a_{12} = N_1 a_1 + N_2 a_2 \qquad (1)$$

(N_1 and N_2 are the mole fractions of the components, a_1 and a_2 are the molecular areas in the pure films at the same surface pressure, and a_{12} is the average surface area of the mixed film).

Negative deviations from the "additivity rule" are observed in the pressure region of 1 and 8 dyn/cm and positive deviations in the region of 25 dyn/cm. A remarkable fact is that at 25 dyn/cm the molecules in the mixed films of N_{VI} = 0.5, 0.35, and 0.25 occupy an average molecular area of approximately 28 Å^2/molecule. This area agrees well with the cross-sectional area of the chromophore obtained from a CPK model of the molecule in the stretched conformation ($a \sim 26$ Å^2). According to this conformation we assume a card-pack-like arrangement of the chromophores, the NO_2 groups immersed into the water and the paraffin chains oriented to the air.

Transfer of Monolayers to Glass Slides. Deposition properties and adherence of monolayers depend strongly on the nature of the solid.[7] Assuming that the weak hydrophilic NO_2 groups of the dye monolayer (N_{VI} = 0.35) are in contact with the subphase, we expect strong attachment to solids with weak

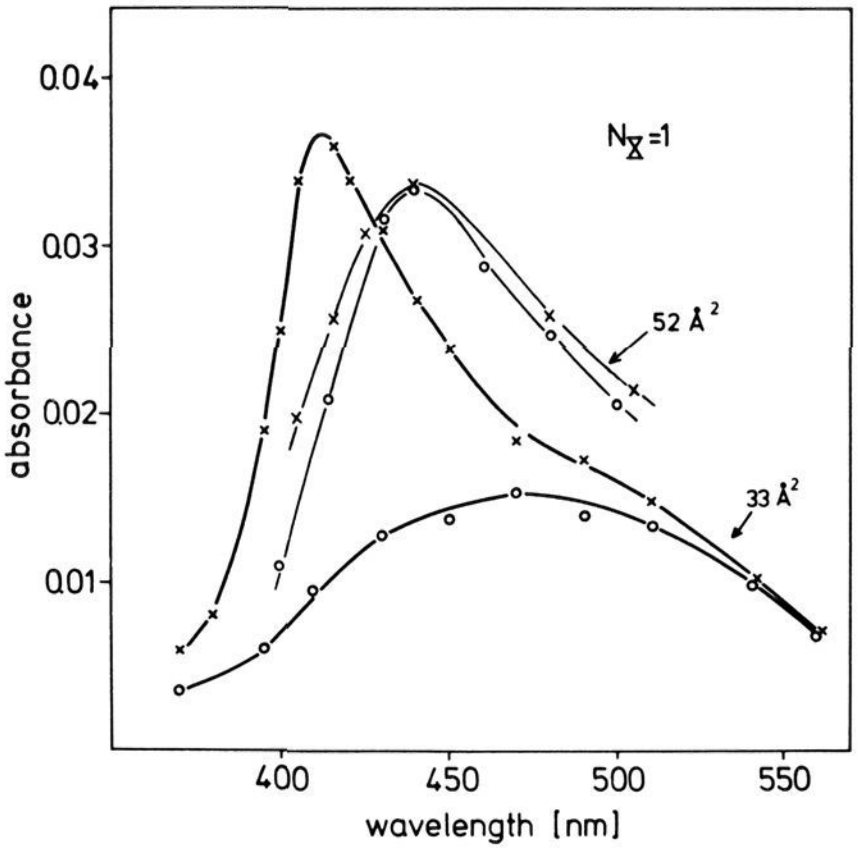

Figure 3. Absorbance spectra of monolayer X on doubly distilled water for a = 52 Å^2/molecule (first condensed state) and a = 33 Å^2/molecule (second condensed state). s-polarized light (—O—O—); p-polarized light (—X—X—).

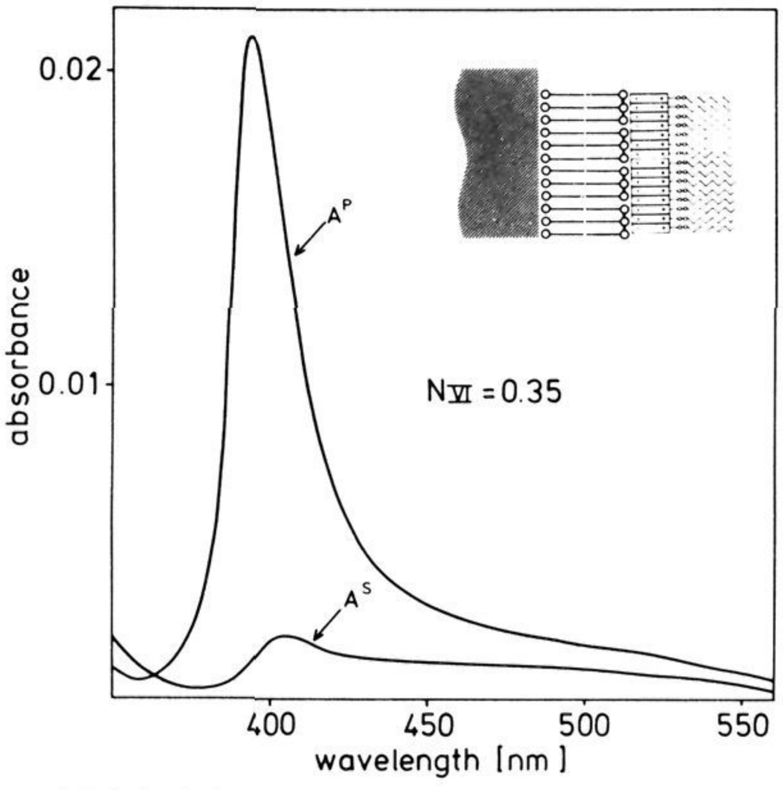

Figure 4. Polarized absorption spectra of the mixed monolayer of dye VI and X, N_{VI} = 0.35, deposited on a tripalmitin layer. The glass plate is successively covered by a Cd-arachidate layer, a tripalmitin layer, and finally a dye layer.

hydrophilic surfaces. Microscope slides of different surface properties were lifted through a dye monolayer covered subphase and the quality of the deposited monolayer (visible dry or wet) and the deposition ratio (one for coherent layers) were observed. Clean glass slides (strong hydrophilic surface) came out wet (deposition ratio = 1) under different transfer conditions. Glass slides which were treated with $Si(CH_3)_2Cl_2$ (hydrophobic surface) came out apparently dry but were covered with visible patches of the monolayer (deposition ratio <1). A suitable (weak hydrophilic) solid surface was obtained by deposition of a tripalmitin monolayer (ester groups) on immersion of a Cd-arachidate layer covered glass slide, on which dry and coherent dye monolayer could be transferred at different transfer conditions (π = 15–25 dyn/cm, raising rate 0.5–2.0 cm/min). It was also possible to construct sandwich-like systems consisting of several quadruple-layer units each of which was composed of two Cd-arachidate, one tripalmitin, and one dye layer (N_{VI} = 0.35).

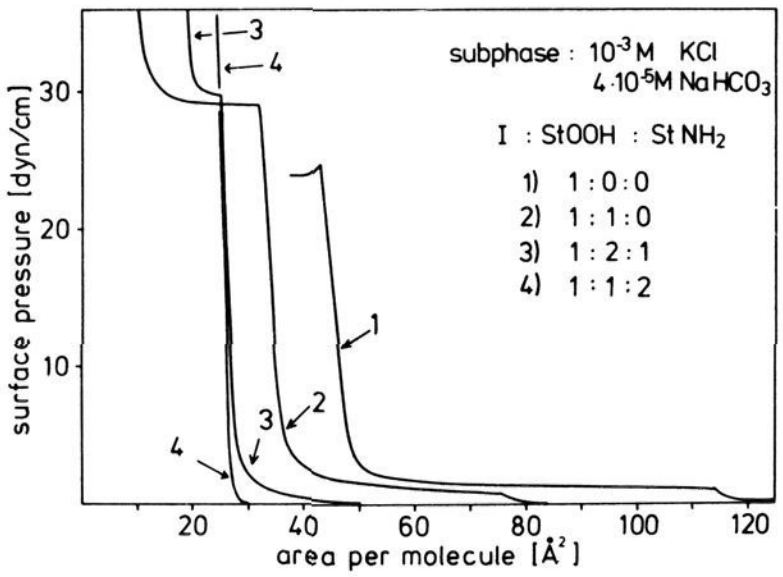

Figure 5. Surface pressure–area plots of dye I and of mixtures of I, stearic acid, and stearylamine on potassium chloride subphase at pH 6.6; t = 21–22 °C. Abscissa: average molecular area.

In case of glass slides covered with one dye layer (initially hydrophilic and hydrophobic surface, respectively) we observed that the dye layer floats off the solid (deposition ratio <0) as the plates were immersed into the fatty acid monolayer covered water.

Absorbance Measurements. For the liquid expanded state at π = 1 dyn/cm the pure and mixed monolayers show equal absorbance spectra which are attributed to monomers (M band) whose chromophoric long axis is randomly distributed in the plane of the monolayer (for details see ref 4). The shape of the absorbance spectra of the condensed films depends strongly on the composition of the mixture. The polarized spectra of dye X recorded at a = 53 Å^2/molecule (first condensed state) *show a blue shift of 30 nm relative to the M band* and a dichroic ratio of one (Figure 3). For the second condensed state (a = 33 Å^2/molecule) an aggregate band (60 nm drifted to the blue relative to the M band) which is accompanied by an M band is found with p-polarized light and a strong M band with s-polarized light (Figure 3). As we turn from the pure film X to mixtures ranging from N_{VI} = 0.25 to 1.0 we observe a drastic decrease of the M band and an increase of the aggregate band which appears at about $\lambda \simeq 400$ nm (H band for N_{VI} = 1; see ref 4). For the special mixture of N_{VI} = 0.35 practically a pure H band is observed with polarized light as illustrated in Figure 4 for a monolayer deposited on a tripalmitin-covered glass slide. These spectra reflect the high degree of order of the designed monolayer, which consists of chromophores in a card-pack-like arrangement, the long axis of the chromophores normal to the layer plane.

2. Three-Component Films Which Contain Dye I, Stearic Acid (STOOH), and Stearylamine ($STNH_2$). Effects of Monovalent Cations on π–a Isotherms. The π–a isotherms of different mixtures are illustrated in Figure 6. Previously it was shown that the plateau region of the π isotherm of the pure monolayer I is associated with a rearrangement of the dye molecules from the edge-on position to the erect position, and that the inflection at high surface pressure indicates a collapse phase of liquid-like nature.[4]

A similar behavior of dye I is found in a mixed film of I and stearic acid (Figure 5, curve 2, molar ratio 1:1). The expected collapse pressure, however, occurs here at 29 dyn/cm, which may be attributed to a weak anchoring effect of the stearic acid. Above 32 dyn/cm the average area approaches 10 Å^2/molecule, indicating a close-packed monolayer of stearic acid with dye molecules squeezed out of the film. If we turn to three-component monolayers (I, STOOH, $STNH_2$), isotherms, which are typical for condensed films, are obtained

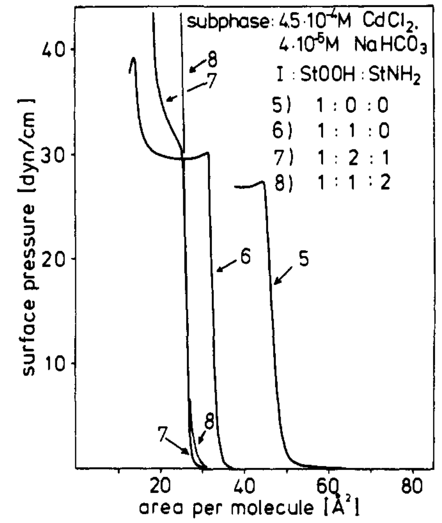

Figure 6. Surface pressure-area plots of dye I and stearylamine and of mixtures of I, stearic acid, and stearylamine on cadmium chloride at pH 6.6; t = 21-22 °C.

(Figure 5, curves 3 and 4). It is interesting to note that for the film composition 1:2:1 a collapse region between 25 and 19.5 Å^2 (average molecular area) is observed, whereas the film 1:1:2 remains stable also above 30 dyn/cm with a limiting area of 25 Å^2/molecule, although the ratio of dye to long-chain fatty substance is equal in both cases. If we assume that the two acids, I and STOOH, compete for the base of $STNH_2$, we obtain in case of film 1:2:1 two-thirds of STOOH and one-third of I being neutralized by the stearylamine. A calculation for the average area according to the assumption that the residual two-thirds of I (the nonneutralized part) is squeezed out gives a_{12} = 18 Å^2/molecule, which is in good agreement with the experimental result.

In case of film 1:1:2 the total acid part is neutralized by $STNH_2$ and anchored by the attraction of the head groups. The calculated average area under this condition is 25 Å^2/molecule and equal to that obtained from the isotherm. A similar behavior is observed for "neutralized films" of other composition.

Effect of Cd Ions on π-a Isotherms. As previously described, Cd ions cause condensed and rigid monolayers of long-chain fatty acids and of dye I which are attributed to strong attraction between the bivalent cations and the carboxyl groups. For that reason it is not surprising that the π-a curves of the mixed films (Figure 6) do not exhibit a plateau region at 1 dyn/cm as observed with monovalent cations. But at high surface pressures the π-a isotherms show a similar behavior as for KCl subsolutions. From this we conclude that the expanded state of the monolayer favors the interaction with Cd ions, whereas in the condensed state the interaction between the negatively and positively charged head groups predominates.

Absorbance Measurements. Neutralized films (molar ratio of $STNH_2$:STOOH + I = 1:1) and transferred by lifting a glass slide (covered with Cd-arachidate layers) through the film from water to air. In this way the mixed dye films came out dry and coherent (transfer ratio $\simeq$ 1, surface pressure = 20 dyn/cm). Multilayer systems are obtained by successive deposition of fatty acid monolayers (glass plate moves downward into the water, symbolized by $\downarrow$) and mixed dye monolayers of different composition (glass plate moves upward out of the water, symbolized by $\uparrow$). Polarized spectra of deposited pure dye films and of mixed films of I-STOOH up to a molar ratio of 1:50 are not depicted because they have similar features to those of the condensed monolayer I at the air-water interface published in ref 4, Figure 7 (p-polarized band, λ_{max} 415 nm; s-polarized band, λ_{max} $\simeq$475 nm). Striking spectral changes are observed with deposited three-component films as shown for film compositions ranging from 1:3:4 to 1:49:50 in Figure 7. With decrease of dye concentration the red shift of the p-polarized bands increases and the relative intensity of the s-polarized bands decreases and becomes practically zero at a film composition of 1:15:16.

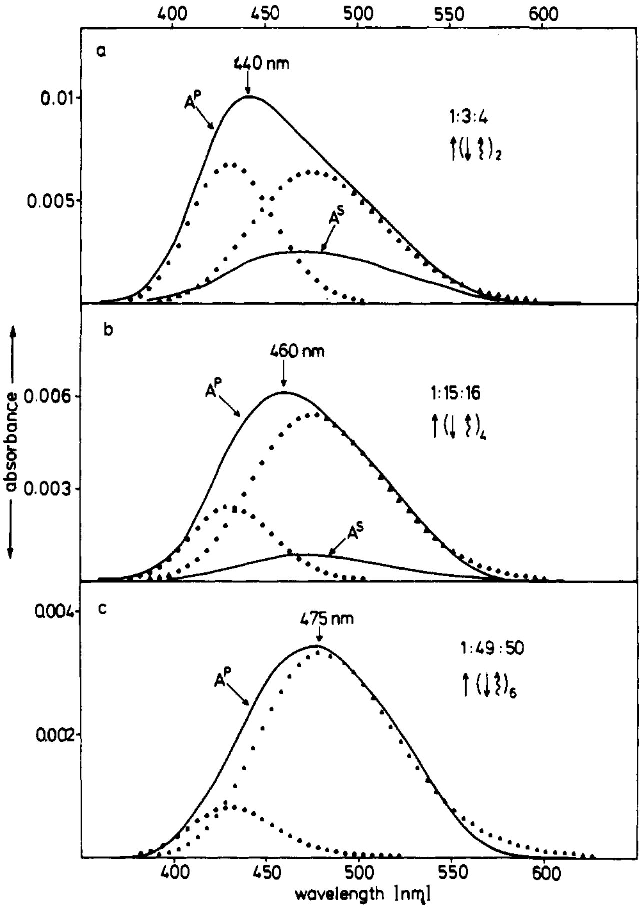

Figure 7. Polarized absorption spectra of mixed layers of 1-STOOH-$STNH_2$ deposited on a glass plate: (a) molar ratio 1:3:4, two dye layers; (b) molar ratio 2:15:16, four dye layers; (c) molar ratio 1:49:50, six dye layers. (·····) Calculated Gaussian curve for the dimer band; (triangles) calculated Gaussian curve for the monomer band.

The absorption bands obtained with s-polarized light are assigned to monomers whose molecular long axis has no preferential orientation (surface concentration σ_i).[4] The p-polarized spectra of monolayers of relatively high dye concentration give rise to the assumption that the dye molecules with molecular long axis normal to the layer plane exist as one part monomers, M^p (surface concentration σ_{M^p}), and one part H aggregated, H^p (surface concentration σ_{H^p}). For obtaining quantitative information on the association number of dyes in aggregates, the p-polarized spectra seem to be particularly suitable for analysis. The total surface concentration of the dye in the film, σ, is given by the π-a curve at the surface pressure used for film deposition:

$$\sigma = \sigma_i + \sigma_{M^p} + n\sigma_{H^p} \tag{2}$$

where n is the association number of the aggregate. If we assume that the monomers M^p are in equilibrium with essentially a single aggregated species H^p, $nM^p \rightleftharpoons H^p$, the mass action law can be applied:

$$K = \sigma_{H^p}/(\sigma_{M^p})^n \tag{3}$$

$$\log (n\sigma_{H^p}) = \log (nK) + n \log \sigma_{M^p} \tag{4}$$

where K is the association constant. Hence a plot of log ($n\sigma_{H^p}$)

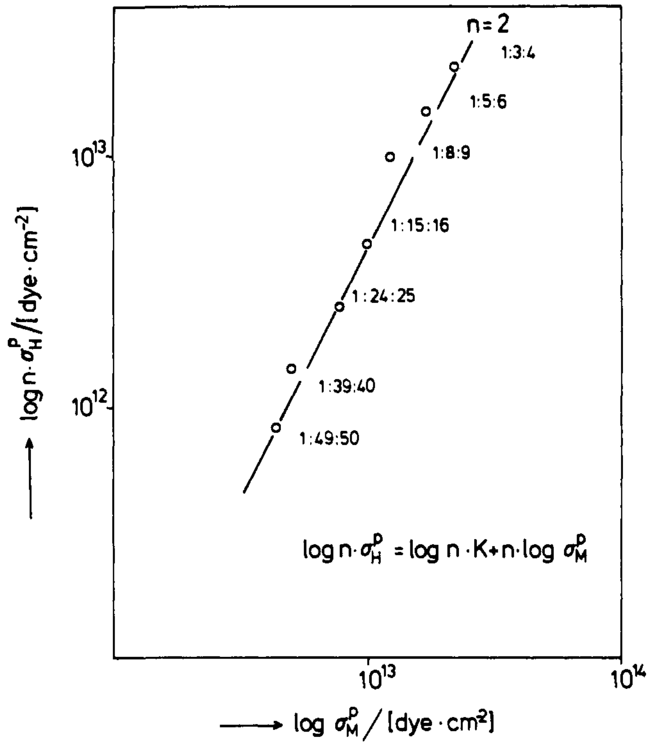

Figure 8. Plot of log ($n\sigma_H{}^p$) vs. log $\sigma_M{}^p$ for different film mixtures of I-STOOH-STNH2. The solid line is drawn with theoretical slope of 2. For details see text.

vs. log $\sigma_M{}^p$ should be linear with a slope of n and an intercept allowing the evaluation of K.

The oscillator strength of the n aggregate is assumed to be n-fold that of the monomer.[8] Therefore we can write for the area under the absorption curve

$$\int A^s(\nu)\,d\nu = \text{const}\ \sigma_i \qquad \text{s-polarized light} \qquad (5)$$

$$\left.\begin{aligned} \int A_M{}^p(\nu)\,d\nu &= \text{const}\left(\sigma_i + \frac{3\sin^2\alpha}{n_F{}^2}\sigma_M{}^p\right) & (6)\\ \int A_H{}^p(\nu)\,d\nu &= \text{const}\left(\sigma_i + \frac{3\sin^2\alpha}{n_F{}^2}n\sigma_H{}^p\right) & (7)\end{aligned}\right\}\ \text{p-polarized light}$$

where $A(\nu)$ is the absorption as a function of the frequency ν, s and p stand for s-polarized and p-polarized, and M and H stand for monomer and H aggregate, respectively. For the used angle of incidence $\alpha = 45°$ and with an estimated refractive index of the dye film of $n_F = 1.60$ we obtain for $(3 \sin^2 \alpha)/n_F{}^2 = 0.59$.

From eq 2 and 5-7 we find

$$\sigma_M{}^p = \frac{\int A_M{}^p(\nu)\,d\nu - \int A^s(\nu)\,d\nu}{\int A_H{}^p(\nu)\,d\nu + \int A_M{}^p(\nu)\,d\nu - 0.41\int A^s(\nu)\,d\nu}\,\sigma \qquad (8)$$

and a corresponding equation for $n\sigma_H{}^p$. The contour of the p-polarized bands is approximated by two Gaussian curves, one for the M band and one for the aggregate band.

$$A^p(\nu) = A_H \exp\left[-\frac{1}{2}\left(\frac{\nu - \nu_H}{\Delta\nu_H}\right)^2\right] + A_M \exp\left[-\frac{1}{2}\left(\frac{\nu - \nu_M}{\Delta\nu_M}\right)^2\right] \qquad (9)$$

The maximal values of the aggregate band, A_H and of the M band, A_M, are located at ν_H and ν_M, respectively, while their width is denoted by $\Delta\nu_H$ and $\Delta\nu_M$, respectively.

With the values $\nu_H = 6.977 \times 10^{14}\ s^{-1}$ (λ_H 430 nm), $\Delta\nu_H = 0.364 \times 10^{14}\ s^{-1}$, $\nu_M = 6.316 \times 10^{14}\ s^{-1}$ (λ_M 475 nm), and $\Delta\nu_M = 0.481 \times 10^{14}\ s^{-1}$ and adjusted values of A_H and A_M, a practically complete fit is reached for film mixtures ranging from 1:49:50 to 1:3:4 (see Figure 7). According to eq 8, $\sigma_M{}^p$ and $n\sigma_H{}^p$ can be calculated. The result is depicted in Figure 8. A straight line is fitted to the circles, whose slope according to eq 4 is $n = 2$. For this reason we conclude that dimers and monomers are in equilibrium. The association constant is evaluated as 2.2×10^{-14} cm^2/dye molecule. The p-polarized spectra of higher dye concentration (e.g., that of 1:2:3, and of the pure film) cannot be sufficiently approximated by the parameters given above. This fact can be explained by a significant formation of trimers or tetramers which requires a third or fourth Gaussian curve.

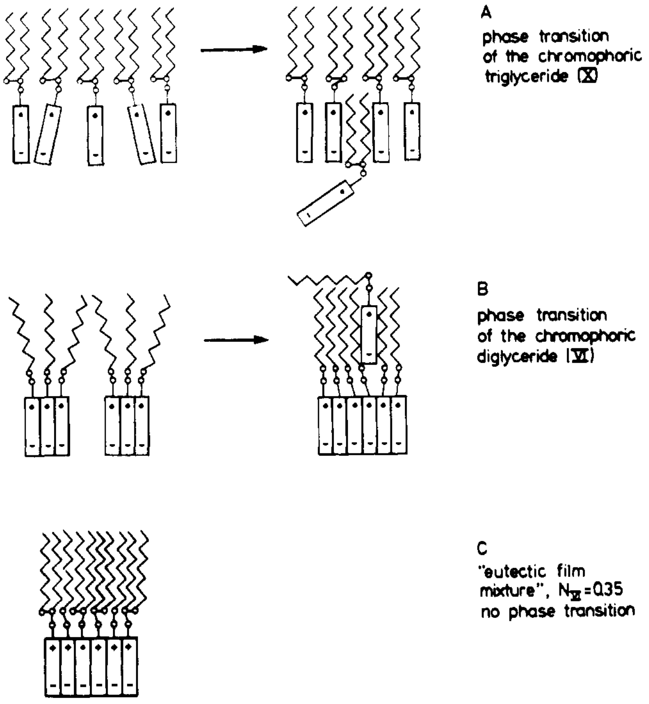

Figure 9. Schematic drawing of the molecular arrangements for different film states. (A) The first condensed state of film X is characterized by closely packed hydrocarbon chains and randomly packed chromophores. At high surface pressure hydrocarbon chains are squeezed into the chromophoric layer by which the film becomes rigid. (B) The first condensed state for film VI is characterized by loosely packed hydrocarbon chains and closely packed chromophores. At high surface pressure chromophores are squeezed into the hydrocarbon layer producing a rigid monolayer. (C) In case of the special film mixture of $N_{VI} = 0.35$ the cross-sectional area of the chromophore is just equal to the average cross-sectional area of the paraffin chains and therefore a rearrangement does not occur at high surface pressure.

Discussion

In part 1 we have supposed that in the first condensed state of the pure film VI the diglyceride molecules are arranged to bi- or multimolecular two-dimensional associates where the chromophores are vertically aligned with respect to the surface, the paraffin chains are randomly intertwined, and the glycerol group is hydrated. The transformation to the second condensed state was interpreted as dehydration of the polar groups and rearrangement of the molecules into a close-packed monolayer.

In view of the two paraffin chains of molecule X whose cross-sectional area of 40 Å^2 is almost twice that of the chromophore, an organization to H aggregates is prevented. Consequently we expect monomers and probably dimers without preferential orientation for the first condensed state (see schematic diagram in Figure 9A). This hypothesis agrees well with the spectral data ($D = 1$ for λ_{max} 440 nm) and the molecular area of 50 Å^2/molecule at $\pi = 7$ dyn/cm. Assuming dehydration of the polar groups and vertical alignment of the paraffin chains as a result of film compression we expect the second condensed state at $a = 40$ Å^2 ($\pi = 20$ dyn/cm), as found. This fact is not well understood. The model for the molecular arrangement depicted in Figure 9A is indeed consistent with the experimental data but must be considered as suggestive. Only a weak indication of a second phase transition is shown by the π-a curves of $N_{\text{VI}} = 0.75$, 0.5, and 0.25, whereas the π-a curve of $N_{\text{VI}} = 0.35$ rises straightly. This latter behavior may be related to an "eutectic mixture" for which the cross-sectional area of the close-packed chromophores is just equal to the average cross-sectional area of the close-packed paraffin chains (for $a_{12} = 30$ Å^2/molecule at $\pi = 10$ dyn/cm we calculate 18.2 Å^2 for one paraffin chain). The molecules in this close-packed state (Figure 9C) apparently have enough cohesion, which prevents hydration of the glycerol group and expansion at surface pressures > 4 dyn/cm.

As the geometry of the di- and triglyceride-like dyes predestine the architecture of the two-component monolayer, the interaction of the head groups of I, STOOH, and STNH_2 has an important influence on the molecular arrangement of the three-component films. Attraction of the amine group of STNH_2 and the carboxyl group of dye I causes an anchoring effect and prevents in this way the squeezing out of dye molecules at high surface pressures. A further effect of the head-group interaction is the dissolution of the aggregates of I in the film into dimers and monomers which lead to an intimately mixed film. Cd ions have a strong condensing effect on fatty acid monolayers and therefore should favor a lateral demixing of the acid and base components. The analysis of the absorbance spectra, however, shows that a lateral demixing occurs only in case of mixed films of STOOH and I on CdCl_2 subphases; in case of "neutral films" the interaction between the amino and carboxyl groups predominates. We may conclude our study by saying that CPK molecular models and considerations about intermolecular interactions indicate indeed the direction for designed monolayer assemblies, but the main work is still a play of trial and error.

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Study of Electrolytic Solution Process Using the Scaled-Particle Theory. 2. The Standard Entropy of Solvation

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Abstract: A method has been developed to describe the entropy of solvation of ions and electrolytes at different temperatures using the scaled-particle theory in conjunction with the Born charging equation. The treatment is apparently consistent with the assumption that the effective size of an ion in solution does not change significantly with temperature and the Born relationship can accurately describe the electrical part of the solvation thermodynamic functions. The prediction of entropy of hydration by this unified approach is reasonably good at higher temperatures where the solvent hydrogen bonding becomes considerably weak. The treatment has also been applied to several nonaqueous solvents to predict entropy of solvation of electrolytes in these solvents.

Introduction

It has been of consistent interest for scientists to calculate some thermodynamic properties of ions in solution from the first principles, and this has been one of the important objectives of the theory of electrolytes in solution. Although it is true that Debye–Hückel theory and its various modifications provide a description of the change of some thermodynamic functions with electrolyte concentration, the prediction of the absolute free energy or entropy of an electrolyte from basic parameters has only been partially successful. Many attempts have made use of some type of electrostatic model[1-5] frequently based upon the Born equation,[6] but the results cannot be made quantitative for ions in general without a large number of arbitrary constants. At least one author in an excellent review has concluded that continuum theories of ionic hydration based on the Born equation seem to have reached an asymptotic limit of usefulness or applicability.[7] The two stumbling blocks to use of continuum models are obtaining or even defining the ionic radius in solution to the required degree of accuracy and lack of detailed knowledge of the dielectric constant in the vicinity of an ion in solution. A number of features of electrolyte behavior have been qualitatively correlated with a more structurally based model[8] such as the Frank–Wen proposal,[9] but the attractive features of this approach have not yet been translated into a quantitative theory.

Latimer did explore in detail the ability of the continuum theory to predict the relative order of hydration energies among various ions, and was able to construct a simple model involving one arbitrary constant each for cations and anions.[10] It can, however, be demonstrated that such a single constant cannot apply for all ions. Latimer also proposed that the experimental

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