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283. Studies of Oriented Monolayers on Solid Surfaces by Ellipsometry

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(19. VII. 71)

Zusammenfassung. Anhand ellipsometrischer Messungen an orientierten Monoschichten von Cd-Arachidat, Perylen, Tripalmitin und Cyaninen auf aufgedampftem Gold oder auf reinen Silberbromideinkristallen wird gezeigt, dass damit Dicke und optische Konstanten solcher Monoschichten sehr genau bestimmt sowie Rückschlüsse über deren Stabilität (Kristallisation, Assoziationsverhalten, Reorientierung usw.) gezogen werden können.

Das abnormale Verhalten des komplexen Refraktionsindexes der ersten paar Monoschichten lässt auf die Gegenwart von absorbierenden Bereichen an der Grenze zwischen Substrat und Schichtsystem schliessen.

Several authors [1] have shown that the *Drude* relationships [2] are still successful for the interpretation of ellipsometric measurements below and at monolayer[1]) coverage.

The direct relation between ellipticity of fatty acid monolayers spread on liquid surfaces and length of the carbon atom chain of the acid has been demonstrated by *Bouhet* [3]. *Rothen* [4] used multilayers of barium stearate deposited on metal slides to calibrate his ellipsometer. Since then, several optical studies of fatty acid films on various substrates have been undertaken [5]; these generally led to the accurate determination of the optical constants and the thickness of the built-up layers.

It is the aim of this paper to extend these experiments, and to show how oriented monolayers of other organic compounds deposited on gold and AgBr-crystals, can be studied by ellipsometry.

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[1]) Siplified term for 'monomolecular layers'.

Experimental. – a) *Principles of ellipsometric measurements.* Details of this technique are given elsewhere [2].

An absorbing medium is characterized by its complex refractive index $n_c = n - ik$ (where the real part n is the refractive index and the imaginary part k the extinction index). The value of n_c can be determined by ellipsometry, which measures the change in the state of polarization after reflection. By resolving the electric vector of a beam of elliptically polarized light incident to a reflecting surface into two components E_p and E_s (parallel and perpendicular to the plane of incidence), the state of polarization can be defined by the relative phase change Δ between parallel and perpendicular components

$$\Delta = \delta_p - \delta_s \tag{1}$$

and by the relative amplitude attenuation $\tan \psi$

$$\tan \psi = \frac{E''_s / E''_p}{E_s / E_p} \tag{2}$$

(where E'' stands for the electric field amplitude of the reflected wave).

After reflection, the two components of the electric vector are retarded in phase and reduced in amplitude by amounts which are characteristic of the optical properties of the reflecting surface.

Values of Δ and ψ are calculated for different film thicknesses by means of a computer program similar to the one described by *McCracken & Colson* [6].

All the measurements have been made using a *Rudolph* photoelectric ellipsometer (type 43603–200 E) whose optical components were adjusted to $\pm 0.01°$, with quarter wave plates producing elliptically polarized incident light at $\lambda = 5461$ Å (Hg-lamp). A very accurately adjustable specimen holder allowed reproducible positioning of the sample after deposition of the monolayers.

b) *Monolayer technique.* *Kuhn* and coworkers [7] have modified the *Langmuir-Blodgett* [8] technique so as to be able to deposit almost any system of monolayers on solid substrates. (Diffusion of the molecules [9] is avoided by using compounds substituted with long chain paraffin radicals; the ionic character of these molecules is thus modified, giving rise to hydrophilic and hydrophobic parts.) A solution of the dye or the dye mixed with a fatty acid in an organic solvent can then be spread on water, and, after evaporation of the solvent, the surface pressure necessary to obtain a monolayer on the water surface (determined independently for each substance from compression isotherms [10]) is applied. This monolayer can be transferred to the surface of a water insoluble solid substrate by slowly dipping this substrate through the monolayer, and thus organized monolayer systems are realized on the substrate. A detailed description of the techniques used by *Kuhn* and coworkers to create oriented monolayers and to investigate their structure and stability is given in [11]. In our work, we used an automatic arrangement similar to the one described [11], to maintain constant surface pressure of the spread film (to ± 1 dyn/cm) and to measure simultaneously very small changes of the total area. We have realized a controlled transfer of the spread monolayer to a rather small area (1 cm² and less) of the solid surfaces (*e.g.* silver halide monocrystals) by monitoring the changes of the area on the water surface and using a servo-system connected to a *Wilhelmy* balance [11].

As a subphase, a 2.5×10^{-4}M solution of CdCl₂ in quartz bidistilled water (pH 5.6 at 22°C) was used. As previously shown by *X*-ray diffraction of deposited multilayers [11], the Cd salt content of the layer is then about 50%, when pure fatty acids are spread on this subphase. As a spreading solvent, we mainly used methylene chloride (Uvasol *Merck*). Ultrasonic cleaning treatment (as described [11]) was applied to all surfaces in contact with the subphase, and to glass and quartz slides to be covered with monolayers.

c) *Silver bromide crystals.* Pure AgBr was obtained by direct synthesis from 99.999% silver and high-purity bromine, and large (about 1–2 cm ∅) monocrystals of AgBr were produced using a dropping method developed in our laboratories [12]. The purity of the crystals was determined by spark emission spectroscopy (total impurity content $\leqslant 1$ ppm) and by ionic conductivity measurements (5×10^{-8} ohm⁻¹ cm⁻¹ at room temperature). Sections parallel to low index faces ($\langle 111 \rangle$, $\langle 110 \rangle$ and $\langle 100 \rangle$) were cut after orientation by *X*-ray diffraction. These crystals were polished mechanically and then chemically with diluted KCN or Na₂S₂O₃ in order to obtain optically smooth surfaces (mean surface roughness ca. 150 Å).

Results and Discussion

a) *Cd arachidate on vapour condensed gold.* A multilayer system of Cd arachidate/ arachidic acid (50%) on a glass slide covered with a 600 Å layer of vapour condensed gold has been built up by successively depositing monolayers in steps of two. Ellipsometric measurements were made after each two monolayers, at an angle of incidence
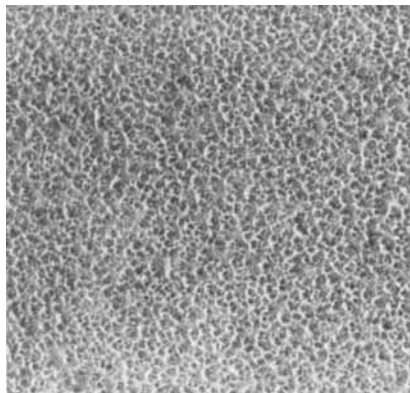

Fig. 1. *Pt—SiO (7°) cone replica of 6 monolayers of Cd arachidate/arachidic acid on glass* (magnification 30,000 ×)
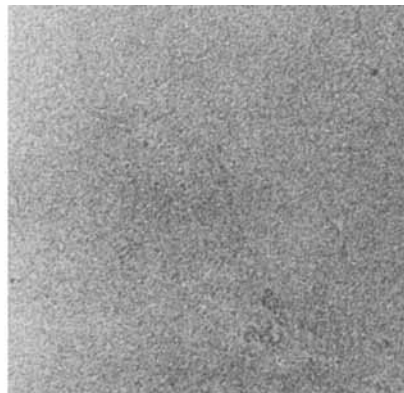

Fig. 2. *Pt—SiO cone replica of 8 monolayers of Cd arachidate/arachidic acid on glass* (magnification 10,700 ×)
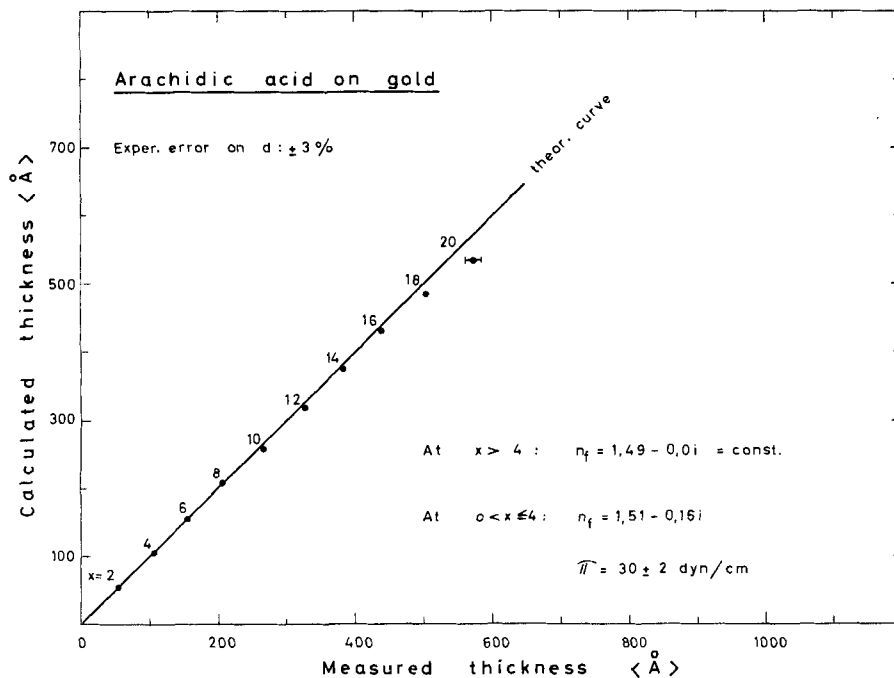

Fig. 3. *Calculated* vs. *ellipsometric film thickness for a multilayer system of Cd arachidate/arachidic acid on evaporated gold* (x, number of monolayers)

of 70° (principal angle: 68° for gold), and at 5461 Å, with the quarter wave plate at a fixed angle of 45°. The electron micrographs shown in Fig. 1 and 2 show that the deposited layers are fairly homogeneous; cracks seldom occurred and holes were practically absent.

Fig. 3 shows a plot of thickness calculated from C–C bond lengths [7] and X-ray diffraction (26.8 Å per Cd arachidate monolayer) *vs.* thickness calculated from ellipsometric measurements using the variation of ψ with thickness. Excellent agreement between calculated and measured thickness is observed up to 18 monolayers[2]). Similar results were obtained when the 'ellipsometric' thickness was derived from the variation of Δ with thickness, although the precision of these measurements is somewhat lower.

As already pointed out by *Partovi* [5b] and later by *Mertens et al.* [5b] no agreement between theoretical and ellipsometric thickness measurements is observed if the uncovered gold surface is taken as a reference to calculate n_c of the substrate. However, by considering as a reference the gold surface covered with four monolayers of Cd arachidate, we obtained excellent agreement with the theoretical thicknesses using a calculated film refractive index of $n_f = 1.49–0.00\ i$ which was assumed to be constant up to 20 monolayers. The calculated complex refractive index corresponding to the first four monolayers of Cd arachidate, $n_{0–4} = 1.51–0.16\ i$, shows that the first monolayers next to the metal surface are not transparent.

Similarly, *Mertens et al.* [5b] using Ba stearate layers on gold, found a strong dependence of the imaginary part k on thickness, varying continously from $k = 1.3$ for the first layer to $k = 0$ for the fourth layer which was then taken as a reference. These authors also showed that this anomalous behaviour of the optical constants within the first few layers is not due to a shortcoming of the *Drude* equations, but rather to the presence of thin absorbing regions at the interface between the dielectric and the metal film. These absorbing regions may be due to adsorbed gases or other impurities. Another possible cause may be the difference of state of binding between the first layer and the metal surface, and between inner and outer layers. In fact, by using ellipsometric measurements based on desorption rate studies of stearic acid from Pt and Ni surfaces, *Pimbley & McQueen* [13] have shown that the binding energy of the outer layers of stearic acid is the same for Ni and Pt (44 kcal/mole) and compares well with the sublimation energy (41.9 kcal/mole), while the binding energy of the first layer in contact with the metal depends on the substrate (36.4 kcal/mole for Ni, 30.5 kcal/mole for Pt) and lies between the sublimation (41.9 kcal/mole) and the vaporization energy (25.5 kcal/mole at 25°C). These results confirm that the first layer in contact with the metal surface exhibits energetic behaviour different from that of the outer layers.

In our calculations, we did not take into account the optical anisotropy of these oriented monolayers. The calculated values of the film refractive index are thus not resolved into their components $n_{//}$ and $n_{\perp}$ (parallel and perpendicular to the substrate). Thickness values are 2% too large if calculated for isotropic layers instead of anisotropic ones (as for the case of Cd arachidate on silicon [14]), and 4% too small for the isotropic layers of a cyanine dye measured at the wavelength of its absorption maximum [14]. Corrections of this order of magnitude would not influence our

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[2]) The deviation from the theoretical curve after x = 18 is real and due to crystallization in the layers, which changes the film refractive index.

measurements within the limits of error indicated in this work. The anomalous optical behaviour within the first monolayers is still observed if corrections for the optical film anisotropy are applied [14].

b) *Cd arachidate on AgBr (111)*. Measurements as in a) have been made on a pure single crystal of silver bromide at an angle of incidence of 60.0° and wavelength of 5461 Å. The deposition of Cd arachidate monolayers in steps of two has been followed by monitoring the changes of the area of the spread monolayer on the subphase during deposition on the crystal, as described above. As shown in Table 1, excellent agreement between calculated and measured thicknesses is again obtained when taking the AgBr surface covered with four monolayers of Cd arachidate as a reference.

Again, the best values for the optically measured thickness are derived from the variation of the relative amplitude ψ with thickness.

A constant film refractive index $n_f = 1.49–0.00\ i$ has been calculated for all except the first four layers, which show a refractive index $n_{0-4} = 1.60–0.28\ i$.

Table 1. *Calculated* vs. *measured thickness of Cd arachidate multilayers on AgBr*

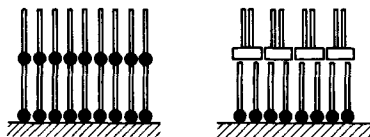| Number of layers deposited	calc. thickness $d_{calc.}$	d from Δ d_Δ	d from ψ d_ψ
4 (reference)	108	108	108
6	161	161	161
8	214	219	219
10	268	273	273
12	322	357	330
14	375	400	383
16	429	444	435

Fig. 4. *Possible structures of Cd arachidate layers*

Furthermore, we could show by ellipsometry that structures like those shown in Fig. 4 (which have been observed when glass was used as a substrate [7]) cannot be realized on AgBr crystals. In fact, if a crystal of AgBr bearing a fatty acid monolayer is dipped through a surface of pure water, this monolayer is again detached from the crystal, and subsequently no fatty acid layer can be added with its (hydrophilic) carboxyl group pointing towards the (hydrophobic) alkyl chain of the (hypothetical) first monolayer. This observation suggests that it is not possible to realize distances of one, three or five fatty acid lengths between the chromophore of a sensitizer and the silver halide surface (see Fig. 4).

c) *Influence of surface roughness on ellipsometric monolayer studies*. In every optical thickness measurement, the problem of the influence of surface roughness on the optical constants should be considered. In order to evaluate to what extent the thickness measurement of a transparent monolayer on a good reflector could be affected, we computed the thickness variation of Δ and ψ with surface roughness for krypton ($n = 1.26$) and for Cd arachidate/arachidic acid ($n = 1.49$) on

silver by using a pyramid model similar to the one described by *Fenstermaker & McCracken* [15] for the computation of the variation of the optical constants of the pure surface with surface roughness. This model is based on the application of the *Clausius-Mosotti* relationship [15] and assumes that the equivalent polarizability of an absorbing material on a rough surface is given by a volume average (variable with the height of growing pyramids for increasing surface roughness) of the substrate and air. The following values (see Table 2) of the complex refractive index n_c as a function of surface roughness of pure silver were considered for our computations [15].

Table 2. *Influence of surface roughness on refractive index of silver*

Surface roughness (Å)	$n_c = n - ik$
0	0.18–3.42 i
50	0.31–2.75 i
100	0.45–2.79 i
200	0.58–2.32 i
300	0.63–2.02 i
400	0.71–1.70 i
500	0.74–1.18 i

Fig. 5 shows the computed variations of $\varDelta$ and ψ with thickness as a function of surface roughness. It follows from these graphs that for both arachidic acid and krypton on silver, $\delta\varDelta/\delta d_t$ equals about the experimental error on $\varDelta$ ($\pm 0.01°$) for a variation in surface roughness of about 150 Å.

Even the rather high difference of 300 Å in the surface roughness between two different silver surfaces would not introduce an error higher than twice the minimal experimental error (determined with our ellipsometer). If optical thicknesses are derived (as is the case here) from the relative
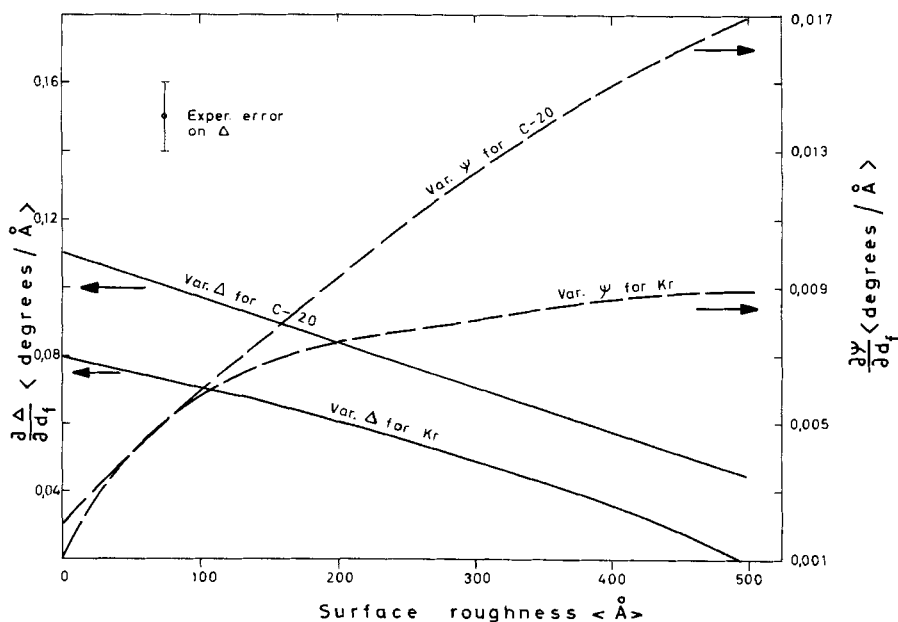

Fig. 5. *Computed variation of the relative phase shift $\varDelta$ and the relative amplitude ψ with film thickness* (d_f) *for krypton and Cd arachidate/arachidic acid* vs. *surface roughness on a substrate of evaporated silver*

amplitude ψ which can be determined to 0.01°, the error on the computed thickness values is still smaller (about twice the experimental error for a roughness variation of 500 Å for arachidic acid). While the sensitivity $\delta\Delta/\delta d_t$ on the relative phase Δ is highest for smooth surfaces, the sensitivity of amplitude measurements increases with surface roughness up to a certain limit. For gold as a substrate the results are not expected to be very different as the variation of the complex refractive index with surface roughness is similar to that of silver [15].

d) *Multilayer systems of other organic compounds on evaporated gold.* As mentioned above, organic molecules other than fatty acids may be applied in stable oriented monolayers if these molecules contain one or several long chain fatty acid substituents and if a slightly modified *Langmuir-Blodgett* technique [11] is applied. A necessary condition for the application of monolayers of an unknown system is the exact measurement of the compression isotherm in order to determine the surface pressure (π) corresponding to the formation of a monolayer on the subphase. Some organic systems exhibit compression isotherms corresponding to the expanded [10] form with a rather small slope. As shown by *Kuhn et al.* [11], this isotherm may be very much improved towards a condensed form curve [10] by mixing the compound with a fatty acid in various ratios.
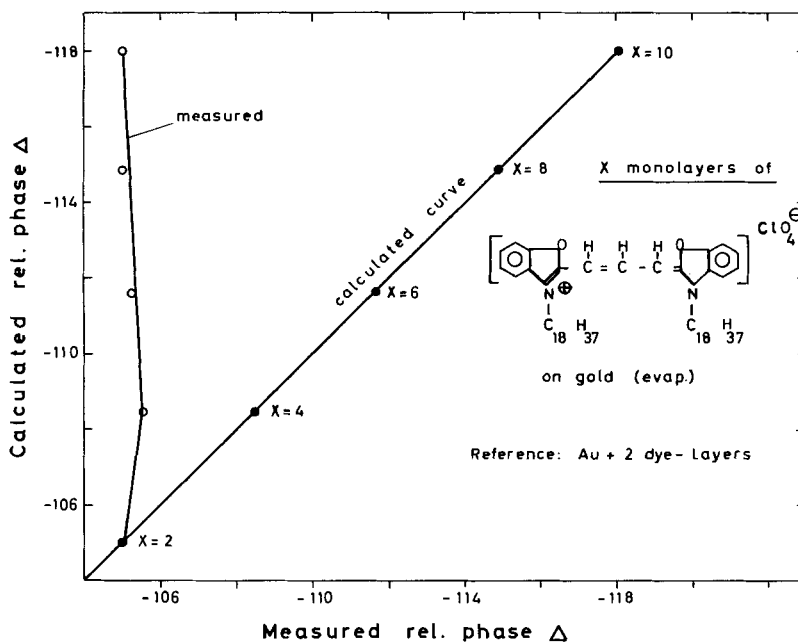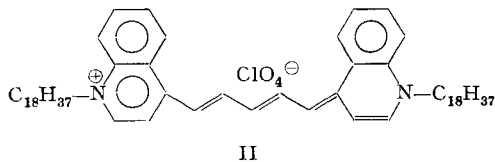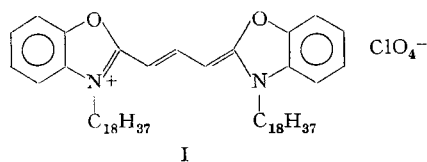

Fig. 6. *Calculated vs. ellipsometric relative phase Δ for a multilayer system of a pure cyanine dye* (formula inserted) *on gold* (x, number of monolayers)

I   II

Monolayers formed this way are often more stable and regular than those obtained by spreading the pure substance on the substrate.

This is illustrated in Fig. 6 which shows ellipsometric results for the carbocyanine dye I applied by the monolayer technique to a vapour condensed gold layer (surface pressure 15 dyn/cm) from a solution of the pure compound in methylene chloride. The measured values of the relative phase shift Δ, which deviate strongly from the calculated curve, show clearly that the pure dye could not be applied in monolayers to the gold surface. When mixed with 10 parts of arachidic acid and applied to the same surface with a surface pressure of 25 dyn/cm, the dye could be normally applied in oriented monolayers, the ellipsometric values being close to the theoretical curve.

As shown by *Kuhn et al.* [16] and later by *v. Szentpaly et al.* [17], the monolayer technique may be very useful in studying the mechanism of spectral sensitization of light-sensitive solids. A necessary condition for this type of experiment is, however, the knowledge of the exact thickness and geometry of these layers. Whenever a new sensitizer is investigated, the conditions under which it can be applied in oriented monolayers are determined very rapidly by ellipsometry, as is shown for the case of the cyanine dye II which sensitizes in the infrared region of the spectrum (sensitization maximum at 870 nm).
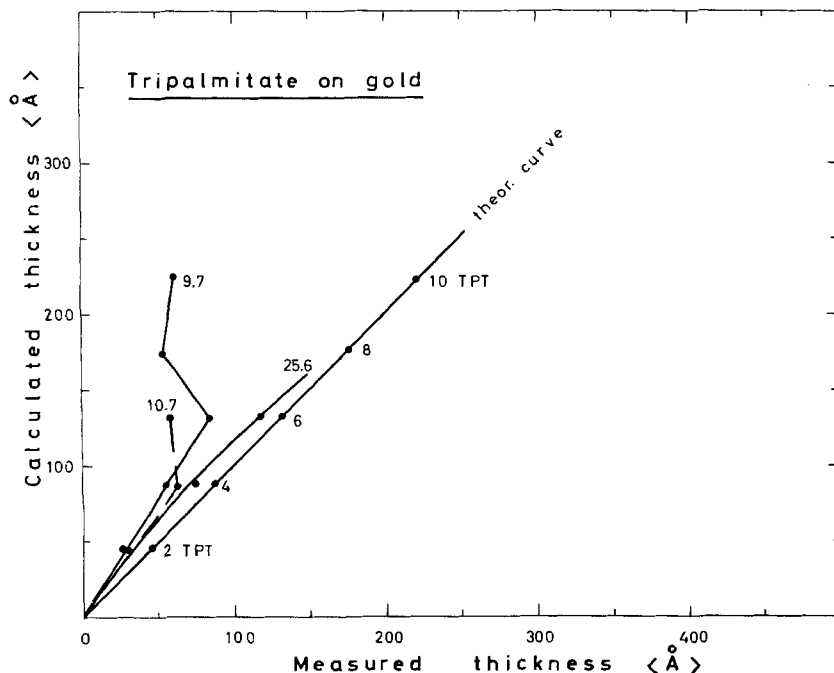

Fig. 7. *Calculated* vs. *measured thickness for a multilayer system of tripalmitoylglycerine* (tripalmitine) *on gold*

The theoretical curve has been calculated for 2, 4, 6 . . . monolayers of tripalmitine. Ellipsometric measurements were made immediately after monolayer deposition (curve 25.6), 15 days later (curve 9.7) and 16 days later (curve 10.7)

Table 3 shows ellipsometric results which have been obtained by applying this compound in monolayers ($\pi = 16$ dyn/cm) on vapour condensed gold, using different ratios of dye to arachidic acid. The calculated thickness (d) is compared with thickness determined ellipsometrically at $\lambda = 5461$ Å and an angle of incidence of 70°, using the pure gold surface covered with two monolayers of the dye as a reference to determine n_c of the substrate.

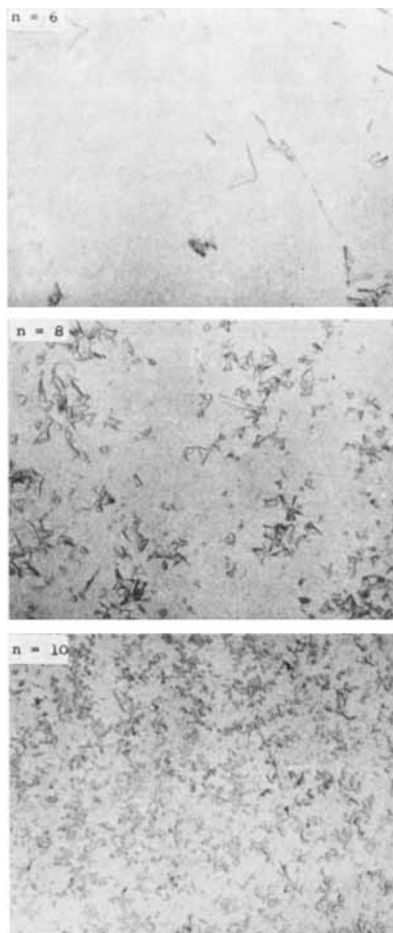Fig. 8. *Polarization micrographs of a tripalmitoyl glycerine multilayer system* (n, number of monolayers) *showing crystallization* (4 mm $= 1 \mu$m)

A constant film refractive index $n_f = 1.46$–$0.10\ i$ has been calculated from our experiments for thicknesses higher than 54 Å (reference value).

As in the previous example, this dye is easily applied in monolayers when mixed with arachidic acid, while the monolayer technique is not applicable to the pure dye under these conditions.

Another useful application of ellipsometry is to control the *stability* of oriented monolayer systems. Frequent measurements within a certain period of time are

Table 3. *Calculated* vs. *experimental thickness of dye II layers*

| Number of monolayers	d (Å) calculated	d (Å) (1:10)	d (Å) (1:5)	d (Å) (pure dye)
2 (reference)	54			
4	108	106	114	86
6	161	168	165	124
8	214	221	224	134
10	268	267	268	166
12	322	342	300	

easily made and deviations from one measurement to the next may be interpreted. An example of an unstable monolayer system is shown in Fig. 7 for tripalmitine (tri-O-palmitoyl-glycerine) on gold. This system showed a significant deviation from the theoretical curve (calculated from $d = 22$ Å/monolayer) already a few days after its formation (graph 25.6, Fig. 7). Two weeks later (graph 9.7 and 10.7, Fig. 7) the ellipsometric thickness deviated still more from the calculated thickness which led us to the conclusion that crystallization was probably occurring within the layers.

This assumption was confirmed by observation with a polarization microscope (Fig. 8) where crystalline aggregates and crystals of 5–10 microns in diameter could be seen on all samples except the uncovered surface.

III
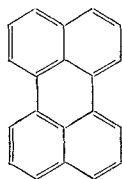
The application of ellipsometry to a dye monolayer system forming small *aggregates* is shown for perylene (III), mixed with arachidic acid. Perylene gives stable mono-layers as shown by *Schreiber* [18]. The geometry of a monolayer of perylene and arachidic acid (shown in Fig. 9) has been established from compression isotherms
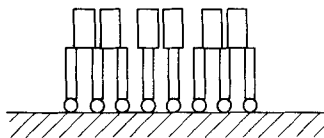
Fig. 9. *Perylene-arachidic acid monolayer*

(which lead to the same molecular area for a dye-arachidic acid mixture as for arachidic acid alone) and from the distance dependence of the photo voltage [18]. From measurements of the dichroism it was concluded [18] that the perylene transi-tion moments are distributed statistically in a direction perpendicular to the surface of the substrate containing the monolayer system. Fluorescence spectra showed an emission at about 580–600 nm when a monolayer system with a low mixing ratio of dye with arachidic acid was excited at 366 nm. This orange fluorescence is due to the presence of small (ca. 1 μm in diameter) aggregates of perylene molecules in the

monolayer. When the mixing ratio became lower than 1:25, the fluorescence emission spectrum suffered a bathochromic shift, and no aggregates were observed in the microscope [18]. From spectroscopic measurements (broadening of the spectrum) it was concluded that some reorientation within the layers occured during the first few days, but microscopic measurements showed that this was not due to the diffusion of perylene molecules across the fatty acid monolayer [18].

No dye aggregates could be seen in the phase contrast microscope or in the interference microscope when the ratio of dye to fatty acid in the mixture was lower than 1:12. In order to see whether the beginning of aggregate formation could be followed by ellipsometry we have studied the multilayer system perylene/arachidic acid (1:25) on vapour condensed gold. The monolayers were applied at a surface pressure of 30 dyn/cm in steps of two and ellipsometric measurements were made at $\lambda = 5461$ Å and an angle of incidence of 70°. Fig. 10 shows the calculated vs. optical thickness, for two independent experiments. While thickness values derived from the variation of Δ are in good agreement with the theoretical thickness, those derived from ψ deviate strongly from the theoretical curve. We obtained the constant refractive film
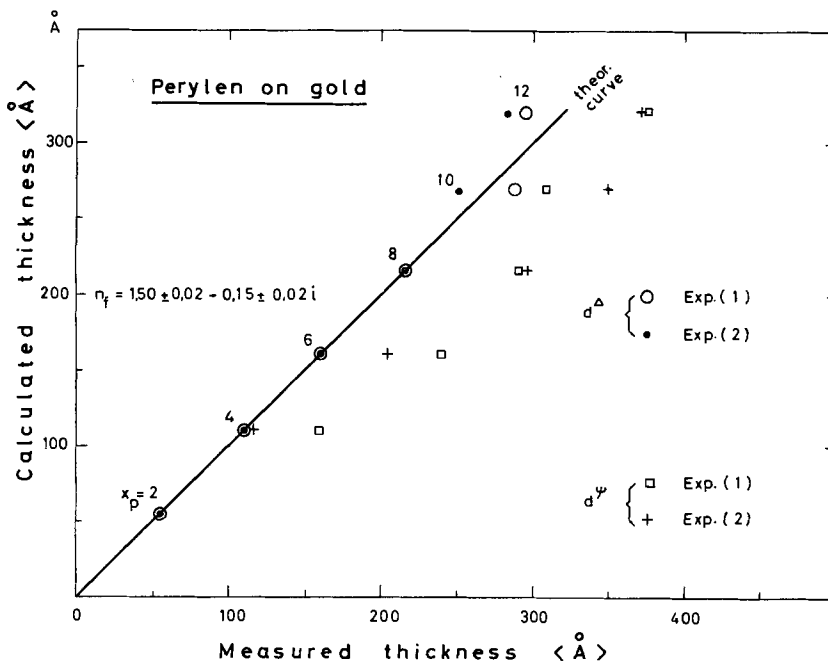
Fig. 10. *Calculated* vs. *ellipsometric thickness of a multilayer system* (x_p, number of monolayers) *of perylene-arachidic acid/Cd arachidate on gold* (1:25)

d^{Δ}; ellipsometric thickness derived from Δ, d^{Ψ}: ellipsometric thickness derived from ψ; n_f, film refractive index for $x_p \geqslant 2$. (Two identical, independent measurements.)

index $n_f = 1.50-0.15\,i$ when the gold surface covered with two monolayers of Cd arachidate was taken as a reference to calculate n_c of the substrate. A value of $n_{0-2} \cong 1.6-0.3\,i$ was computed for the first two monolayers. The fact that the thickness

values (derived from the variation in relative amplitude ψ) deviate strongly from the theoretical curve and are badly reproducible while those calculated from the variation of Δ are in good agreement with expected results show clearly that the imaginary part of the film refractive index (extinction index) is strongly affected when the thickness increases, while the real part (refractive index n) has a constant value up to a thicknesses of 216 Å. A linear dependence of the extinction index k with thickness is calculated (Fig. 11) when k is computed from the *theoretical* thicknesses and a *constant* value of 1.50 for the real part of the film refractive index. As all our ellipsometric measurements were made at a constant wavelength of incident light (5461 Å), this may be equivalent to a displacement of the absorption spectrum with an increasing number of monolayers. We think that the variation of k with thickness is due to the beginning of aggregate formation which finally leads to microscopically visible crystalline aggregates [18] when the dye to arachidate ratio becomes high enough ($\geqslant 1:12$). In our case (dye to arachidate $= 1:25$), no such aggregates could be seen in a light microscope, while in the electron microscope clusters about 50 to 150 Å high and approx. 500 Å in diameter were observed (Fig. 12), which could be small crystalline aggregates of perylene (in layers of pure arachidic acid these clusters were absent [see Fig. 1, 2]).
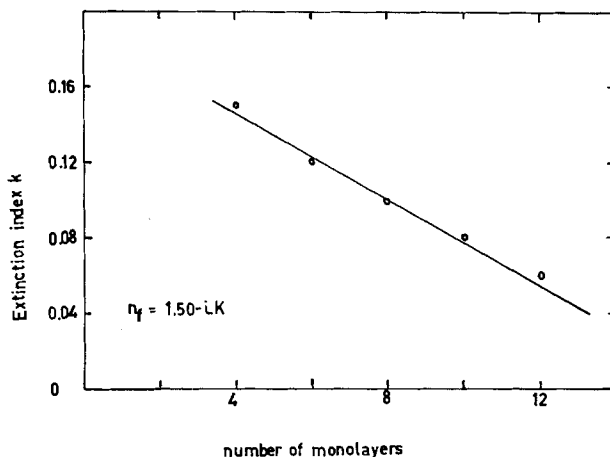

Fig. 11. *Extinction index k vs. number of monolayers for a multilayer system of perylene-arachidic acid/Cd arachidate* $(1:25)$

Computation of k for $n_f = 1.50–ik$ for the case that the film thickness is equal to the theoretical thickness calculated from C—C bond lengths

These results indicate that ellipsometry may be useful for following aggregation in monolayers even before it is measurable by spectroscopic methods.

Reorientation of the perylene molecules within a few days (which had been followed spectroscopically by *Schreiber* [18]) has also been observed ellipsometrically, where we found a decrease in thickness of about 7% after 7–8 days, period after which the thickness became stable. While conclusions concerning the *orientation* of the molecules in monolayers can generally not be drawn from ellipsometric measurements, they are easily drawn by determing spectroscopically the dichroic ratio $D_{//}/D_\perp$ ($D_{//}$ and $D_\perp$ being the absorbance measured with light polarized parallel and perpendicular to the plane of incidence under an angle of incidence of 45°).

Conclusions. – Our experiments show that ellipsometry is useful for the determination of thickness and optical constants of oriented monolayers on various substrates[3]), and the study of stability of these layers and the optimal conditions of their application.
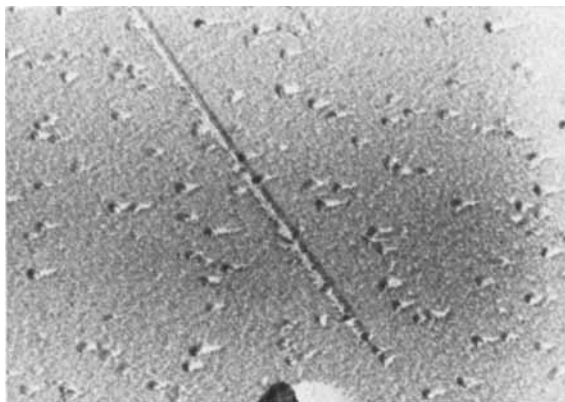

Fig. 12. *Pt–SiO* (10°) *replica of a monolayer of perylene on glass* (magnification 10,000 ×)

Certain precautions must be observed to account for the optical anisotropy of the first two to four monolayers in contact with the substrate. The fact that these layers exhibit a *complex* refractive index even for normally *transparent* compounds suggests the presence of absorbing regions (due possibly to adsorbed layers at the interface). However, if this effect is due to a different state of binding between the substrate and the first layers, ellipsometry would be a useful tool to investigate molecular interactions between a solid surface and an oriented monolayer. Further experiments to interpret these effects are necessary and will be carried out in our laboratories.

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284. Transketolase from Human Erythrocytes Purification and Properties

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(3. VIII. 71)

Summary. Human erythrocyte transketolase (sedoheptulose-7-phosphate: D-glyceraldehyde-3-phosphate glycolaldehyde-transferase) was purified 8200-fold by adsorption onto hydroxylapatite, DEAE-cellulose treatment, acetone fractionation, and chromatography on Sephadex G-100. The purified transketolase could not be separated from glyceraldehyde-3-phosphate dehydrogenase, whereas the latter enzyme could be isolated in a pure state. Its homogeneity is suggested by sedimentation velocity, sedimentation equilibrium, and acrylamide electrophoresis. A molecular weight of 136000 was found. The physicochemical properties of glyceraldehyde-3-phosphate dehydrogenase and transketolase are very similar. A molecular weight of 136000 is suggested for transketolase, although gel filtration with Sephadex G-100 gave only 104000 $\pm$ 10%. This discrepancy is a reflection of an interaction of transketolase with the gel filtration medium. The isoelectric point for transketolase as well as for glyceraldehyde-3-phosphate dehydrogenase, as determined by isoelectric focussing, was found to be around 8.5. The activity of the enzyme is close to the maximum for pH 7.5 to pH 8.6. Additions of thiamine pyrophosphate or other cofactors do not influence the activity. Several divalent cations were tested. Sulfate and phosphate inhibit transketolase approximately to 50% between 50 and 100 mM concentration. Thiamine was present in transketolase, as shown by a microbiological assay and by the thiochrome reaction. The activation energy for the formation of sedoheptulose-7-phosphate from xylulose-5-phosphate was estimated from rate measurements to be 11.2 kcal/mole in the temperature range from 5° to 55°.

Introduction. – Transketolase (EC 2.2.1.1) catalyzes the transfer of a ketol group to a suitable aldehyde acceptor:

$$
\begin{array}{ccccccc}
\boxed{\begin{array}{c} CH_2OH \\ | \\ C=O \end{array}} & & & & CH_2OH & & \\
| & & CHO & & | & & CHO \\
HO-CH & + & | & \rightleftharpoons & C=O & & | \\
| & & R' & & HO-CH & + & R \\
R & & & & | & & \\
& & & & R' & & \\
\text{Donor} & & \text{Acceptor} & & & &
\end{array}
$$