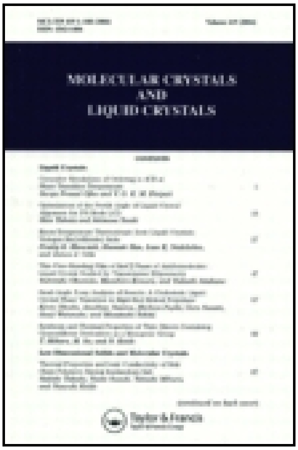

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Liquid Crystal Alignment on Langmuir–Blodgett Films†

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Some initial studies of the liquid crystal aligning properties of LB films of ω-tricosenoic acid, cadmium arachidate and merocyanine dyes have been carried out. These particular materials have been found to induce homeotropic, or tilted homeotropic, alignment in liquid crystal layers. The tilt angle has been measured for alignment on ω-tricosenoic acid and an example of an electrically switched liquid crystal cell using these aligning layers has been demonstrated. Differences have been noted in the uniformity of aligning properties of multilayers of these materials dependent on the packing density of the molecules within the films. In addition it has been found possible to change the alignment of the liquid crystal on ω-tricosenoic acid that has been subject to *e*-beam irradiation.

1. INTRODUCTION

Liquid crystal layers exhibiting uniform orientational alignment over large areas are required in most device applications. The usual methods for obtaining such a preferred orientation rely on inducing various physical and chemical interactions between a prepared substrate and the liquid crystal molecules.

Alignment of liquid crystals on substrates treated with materials such as lecithin[1] and alkoxysilanes[2] have been described previously with some attempt being made to correlate the proposed chemical structure of the organic surface with the subsequent alignment of the liquid crystal. Other studies aimed at optimising the aligning properties of a chrome complex material[3] have highlighted the problems of producing controlled layers of these types of materials on substrates, when using dipping or spin coating techniques to distribute the organic molecules. More recently an investigation of the alignment

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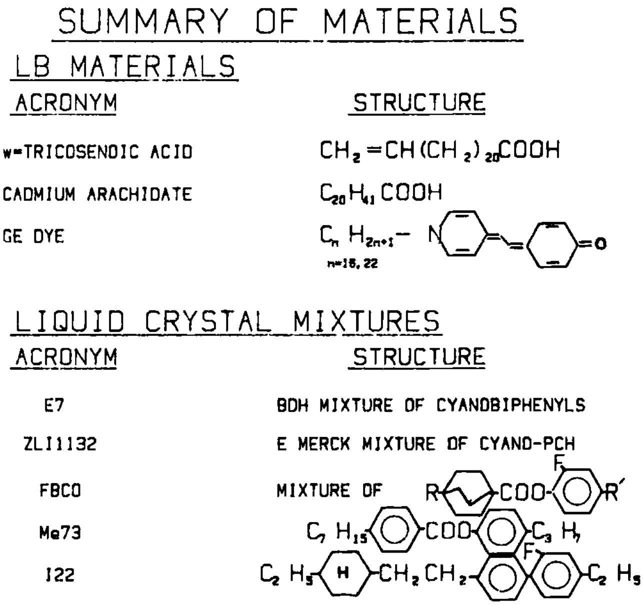
properties of lecithin films deposited using the Langmuir–Blodgett technique has been reported.[4]

The work described here concentrates on the alignment of liquid crystals on some other organic materials which are particularly suitable for deposition by the Langmuir–Blodgett method. Using this technique it is possible to build up monolayer or multilayer films of the chosen organic material with some control over the molecular packing density within the layers. Thus the effect of this factor is accessible to investigation as well as being able to investigate different molecular species.

Results are presented on the aligning properties of monolayer and multilayer films of ω-tricosenoic acid, cadmium arachidate and two merocyanine (GE) dyes. The structural formulae of these materials are shown in Table I together with those of the liquid crystal mixtures used in the experiments. In addition the effect of altering the pressure at which the ω-tricosenoic acid monolayers were prepared is reported. Finally the possibility of altering the liquid crystal alignment on ω-tricosenoic acid by electron beam polymerisation of the LB film is explored.



SUMMARY OF MATERIALS

LB MATERIALS

ACRONYM	STRUCTURE
ω-TRICOSENOIC ACID	$CH_2=CH(CH_2)_{20}COOH$
CADMIUM ARACHIDATE	$C_{20}H_{41}COOH$
GE DYE	

LIQUID CRYSTAL MIXTURES

ACRONYM	STRUCTURE
E7	BDH MIXTURE OF CYANOBIPHENYLS
ZLI1132	E MERCK MIXTURE OF CYANO-PCH
FBCO	MIXTURE OF
Me73	
I22	

FIGURE 1 Anthraquinone-based greenish blue dichroic dyes with a long-wavelength maximum absorption.

2. EXPERIMENTAL

2.1. Preparation of films

The LB films were deposited in a trough of the constant perimeter type held in a clean room environment to limit contamination of the trough by dust. The subphase water was passed through a deionising system containing an activated carbon cartridge to remove organic contaminants and a 0.22 micron filter to remove dust, bacteriological species, etc.

For films of ω-tricosenoic acid the subphase was deionised water with an original resistivity of 18 MΩ cm^{-1} while for cadmium arachidate films the subphase contained cadmium chloride with $[Cd^{2+}] = 2.5 \times 10^{-4}M$ with the pH maintained at ≈ 5.8 by addition of HCl or NaOH. Monolayers of the merocyanine dyes were prepared on a subphase containing $10^{-3}M$ of $(NH_4)_2SO_4$ with the pH maintained at ≈ 7.6.

The substrates used in these experiments were commercially available indium tin oxide (ITO) coated glass with a resistivity in the range of 10–20 ohms/☐ supplied by EEV, Chelmsford Essex. The glass was cut to a size of 75 mm by 12 mm and subjected to a rigorous cleaning procedure involving scrubbing in detergent (Decon 75), rinsing in ultra pure water and a final cleaning in solvents such as isopropyl-alcohol or chloroform. As a final step in the process, just prior to use, the substrates were subjected to a low pressure rf discharge, rinsed in pure filtered water and blown dry in filtered nitrogen. In spite of these precautions contaminant debris was still apparent on some of the substrates which affected the uniformity of the LB films deposited subsequently.

Solutions of ω-tricosenoic acid and arachidic acid were made to a concentration of 0.2 $mg \cdot ml^{-1}$ in Aristar grade chloroform while solutions of the merocyanine dyes were in a mixture of nine parts n-hexane to one part ethanol. The sample materials were then spread on the subphase using a clean, all glass, syringe. After a short time lapse to allow for solvent evaporation the monolayer was compressed at a rate of approximately 0.2 $Å^2$ $molecule^{-1}$ sec^{-1} until the required surface pressure was attained. The substrates were immersed in the subphase before spreading the monolayer and transfer of the first layer occurred on the upward movement of the substrate. The first layer was deposited at a drawing speed of approximately 3 $mm \cdot min^{-1}$ while subsequent layers were deposited at approximately twice this speed.

2.2. Cell Fabrication

For the initial investigation of the alignment properties of the LB samples the liquid crystal cell construction was as shown in Fig. (1). The LB substrate formed the bottom plate of the cell while the top plate was provided by a microscope slide coated with a chrome complex material $(C_{17}H_{35}COO\ (CrCl_2)_2\ OH)^5$ to give a homeotropic surface alignment. This was necessary to provide a controlled top surface to the cell allowing the effect of the LB film on the liquid crystal orientation to be seen clearly. The cell was assembled and spaced with 10 μm polyester strips placed along the short edges. It was clipped together and capillary filled with the chosen nematic liquid crystal material. Care was taken throughout not to touch, and thus contaminate, the inside surfaces of the cells.

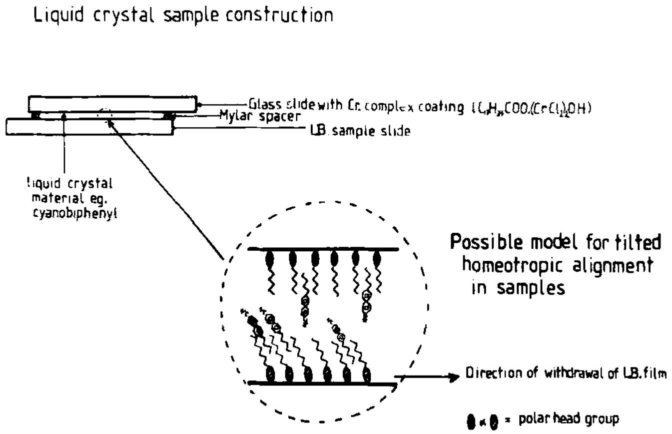


FIGURE 1 Liquid crystal sample construction.

2.3. Tilt angle measurements

In order to measure the tilt angle induced in the liquid crystal orientation by the LB film, a conoscopic technique was used. To improve accuracy this required that the sample cell exhibit a uniform tilt profile across its thickness. Hence cells were assembled using two LB coated substrates arranged with their withdrawal directions anti-parallel. The cells were typically 50 μm thick, in order to maximise the number of fringes visible in the conoscopic figure. It was necessary to leave the cell for some time after filling for a uniform orientation to be stabilised by the boundaries in this thickness of cell.

The sample was viewed between crossed polarisers in convergent white light using a Nikon POH II microscope. The area of the film to be investigated was examined first in orthoscopic mode and the Bertrand lens was subsequently swung into position allowing the conoscopic figure to be viewed. The form of the figure was noted in most cases to be similar to that of a uniaxial crystal cut parallel to its optic axis.[6] Any tilt angle was calculated, using Mullard's Rule, from the displacement of the centre of this unaxial cross from the centre of the field of view. The objective used in the measurements had a long working distance and a numerical aperture of 0.6, corresponding to a conoscopic angle within the liquid crystal of 23.6°, calculated by taking the ordinary refractive index of the liquid crystal to be ~ 1.5.

3. RESULTS

3.1. ω-tricosenoic acid

Monolayer and multilayer films of ω-tricosenoic acid were prepared at a pressure of 30 $\text{mN} \cdot \text{m}^{-1}$ and were examined in 10 μm thick cells containing the material E7. The overall alignment appeared to be a tilted homeotropic with some background structure present in all cases. An example of a typical zero to monolayer interface is shown in Fig. (2), where the edge of the film is clearly defined and the ITO can be seen to give a random, if somewhat granular, alignment to the liquid crystal. The roughness of the alignment on the ITO was an order of magnitude smaller in scale than the background structure seen in the ω-tricosenoic acid films. There were also distinct interfaces visible between regions of the cell containing different layer thickness; see for example Fig. (3). The amount of background structure seen in these multilayers was not reproducible and depended on substrate cleanliness and film quality.

The magnitude and direction of tilt was measured in antiparallel, monolayer LB substrate cells containing E7. It was found to be approximately 4° from homeotropic in the direction opposite to that of the substrates withdrawal from the trough (see Fig. (1)).

Monolayer LB samples of this material were prepared also at pressures of 5, 15 and 20 $\text{mN} \cdot \text{m}^{-1}$. All these samples appeared similar in background structure and liquid crystal aligning properties, to those drawn at 30 $\text{mN} \cdot \text{m}^{-1}$. In addition the tilt angle was measured and found to be 4° from homeotropic in all cases.

10 μm thick cells using a single monolayer substrate were filled with the other nematic liquid crystals shown in Table I. In all cases a tilted

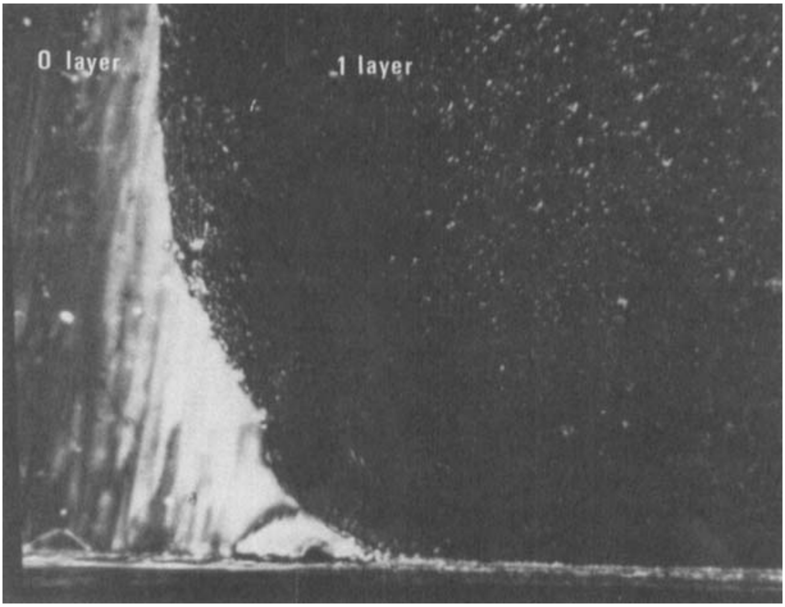


FIGURE 2 Typical zero to monolayer interface in ω-tricosenoic acid sample.

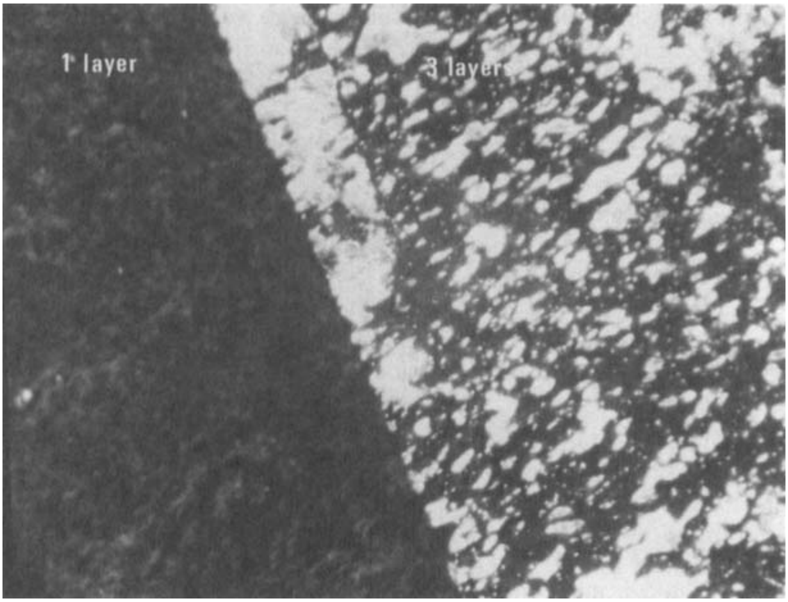


FIGURE 3 Typical monolayer to trilayer interface in ω-tricosenoic acid sample.

homeotropic alignment resulted with the tilt angle appearing similar in magnitude to that measured for E7. There was some tendency for the dialkyl materials to be aligned less well by these substrates than the cyano materials, it being easier to disrupt the alignment by disturbing the cell eg. squeezing it.

An anti-parallel substrate cell of 10 μm thickness was filled with a mixture of the negative dielectric anisotropy host FBCO, which had been doped with about 1% of a blue anthraquinone dye[7] with an optical order parameter of 0.7. The overall alignment of this cell was again tilted homeotropic and application of an alternating voltage of about 10V, caused the liquid crystal layer to realign uniformly with the director parallel to the withdrawal direction; as seen by the stronger absorption of the cell for light polarised parallel rather than perpendicular to this direction. If, instead, the substrates were assembled parallel, so that there was zero tilt in the centre of the cell, application of the voltage produced a more uniform absorption and hence, by inference, a random orientation of the director.

Some monolayer and trilayer samples were exposed to an electron beam to investigate the effect of the reported *e*-beam polymerisation of this material[8-9] on liquid crystal alignment. Irradiation was carried out using a Philips PSEM scanning electron microscope under a vacuum of $\sim 10^{-6}$ Torr. The beam spot size was 320 Å while a typical value of the accelerating voltage was 25 kV and total exposure was of the order of 100 $\mu\text{C} \cdot \text{cm}^{-2}$.

As reported previously[10] the effect of the *e*-beam on the trilayer films was to increase the tilt angle away from the homeotropic, as can be seen by the example in Fig. (4). In monolayer films the effect of exposure appeared to depend on film quality. It was found possible to remove material so that the underlying structure of random alignment on the ITO became visible. At lower exposures the behaviour of the irradiated areas appeared similar to the trilayer samples. As yet no exact value of the increase in tilt has been measured, due to the small areas of the *e*-beam exposure used so far.

3.2. Merocyanine (GE) dyes

Two examples of merocyanine dyes were prepared in LB film form from monolayers on the subphase at a pressure of 28 $\text{mN} \cdot \text{m}^{-1}$. These C_{16} and C_{22} chain length materials both gave a true homeotropic alignment for E7, as seen from the invariance to cell rotation of the conoscopic figure, in monolayer and multilayer films up to the maximum number prepared (53). No interfaces were visible

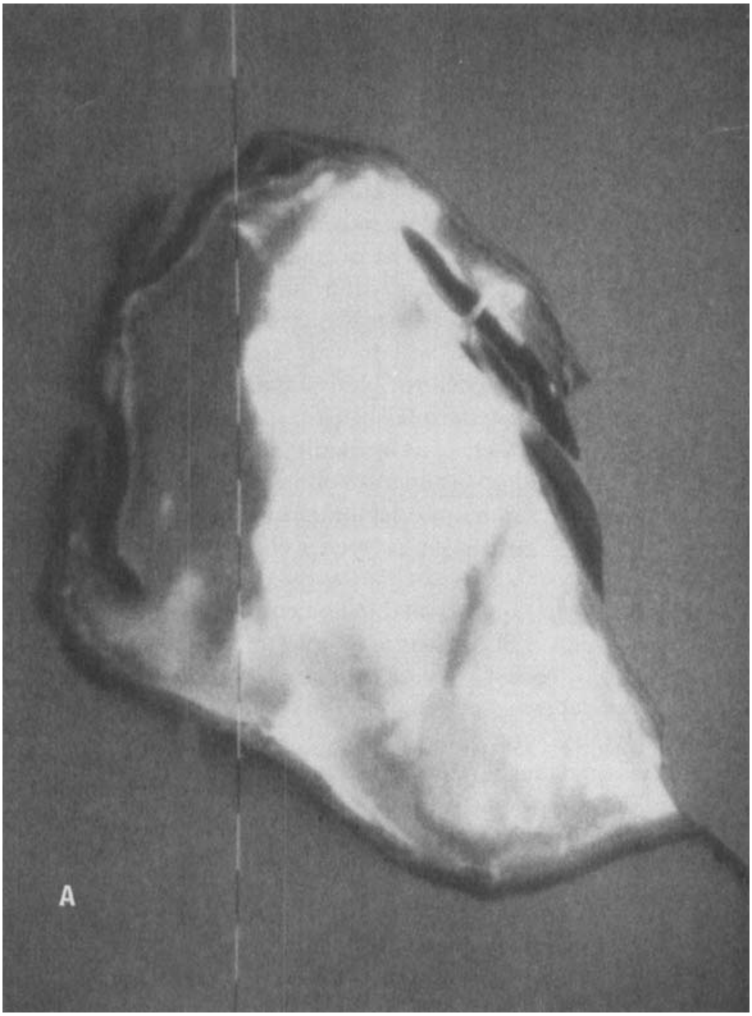
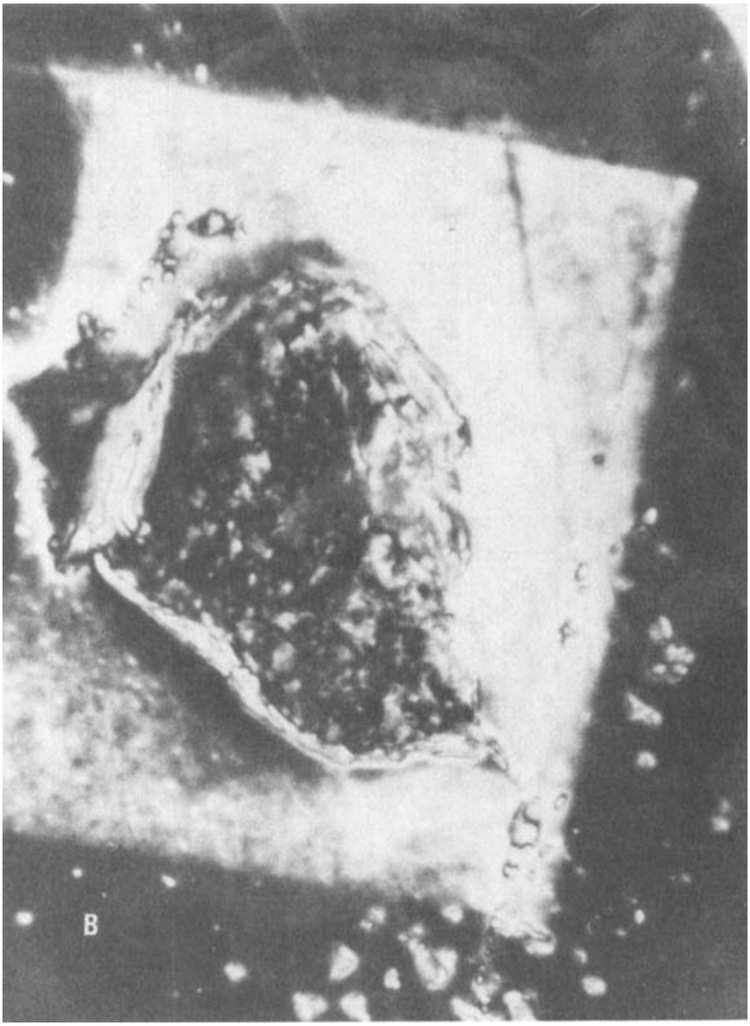


FIGURE 4 Effect of *e*-beam irradiation of ω-tricosenoic acid on liquid crystal alignments, (a) feature on film seen with electron microscope (b) same area in assembled liquid crystal cell.

at the boundaries between the different layer regions and no background structure was seen in the films.

3.3. Cadmium arachidate

Monolayer and trilayer films of cadmium arachidate were prepared at a pressure of 30 $mN \cdot m^{-1}$. The monolayer region gave a tilted



homeotropic alignment to the E7 cell which was similar in magnitude to that observed for ω-tricosenoic acid. The trilayer region was easily distinguished from the monolayer (Fig. (5)) giving a more tilted alignment to the liquid crystal and featuring a periodic defect structure running parallel to the meniscus and perpendicular to the drawing direction. *These "striations" may indicate differences in the* packing or orientation of the molecules of the film.

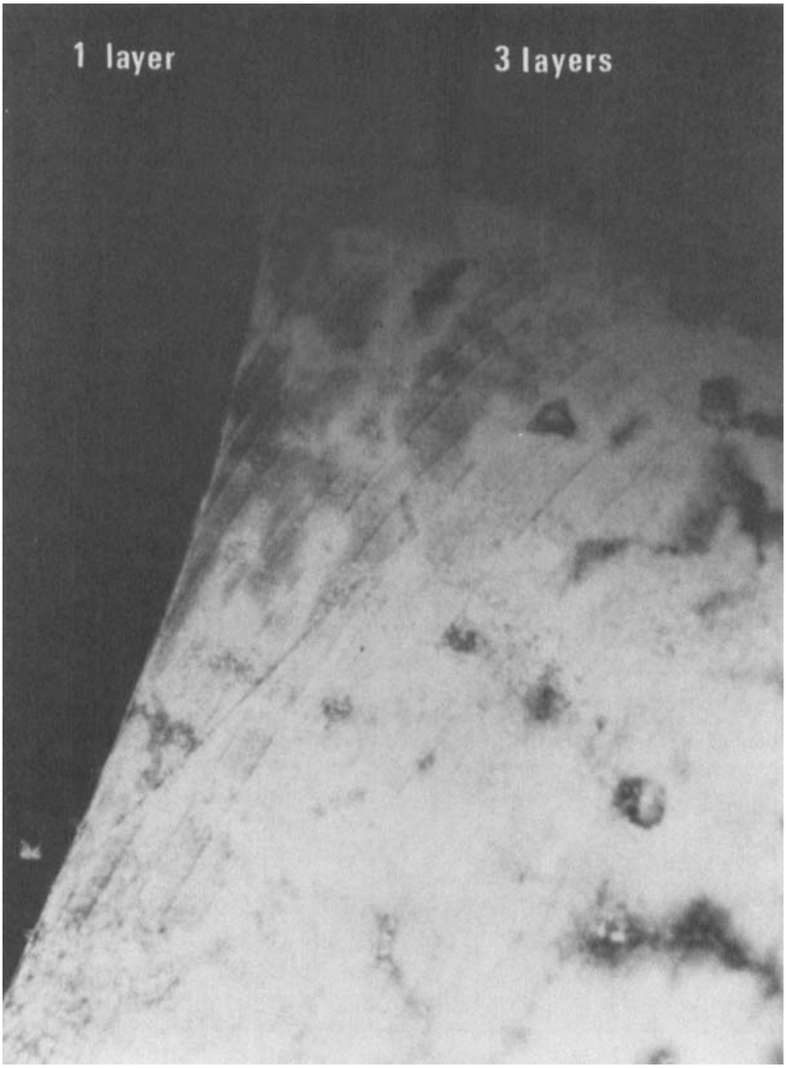


FIGURE 5 Monolayer to trilayer interface in cadmium arachidate showing "striations" in trilayer region.

4. DISCUSSION

The materials examined so far in LB film form are structurally similar to other surfactant molecules used to give homeotropic alignment in liquid crystal applications. That is they have a polar head group, for bonding to the glass, and a long alkyl chain that is supposed to interact with the liquid crystals.[11]

The 4° tilted alignment observed on the ω-tricosenoic acid is interesting and must be linked to the LB process depositing the molecules onto the substrate with their alkyl chains tilted at some angle along the withdrawal direction. This amount of tilt appears to be sufficient to break the degeneracy in the realignment of the dyed negative $\Delta\epsilon$ nematic cells, producing the observed uniform response. The observation that this value of tilt is not altered by lowering the pressure, and hence packing of the molecules in the film, may not be that surprising since, looking at the isotherm in Fig. (6), it can be noticed that the ω-tricosenoic acid monolayer is very condensed, and an increase in pressure from 5–30 $\mathrm{mN \cdot m^{-1}}$ only decreases the average area per molecule from 23 $\mathrm{\AA^2}$–20 $\mathrm{\AA^2}$.

In contrast the isotherm of the merocyanine dye shows that the molecules, and hence the alkyl chains, in these films are more loosely packed. This may contribute to the more perfect homeotropic alignment observed in these films and the lack of any background crystalline structure. It would be of interest to produce films of these materials at different pressures as there is a greater potential for varying the molecular packing than in ω-tricosenoic acid.

Work is continuing at RSRE on this topic and it is planned to investigate other materials with different polar head groups. In addition it is possible to prepare LB films of materials that produce an aromatic surface and thus investigate the aligning properties of this different kind of chemical surface.

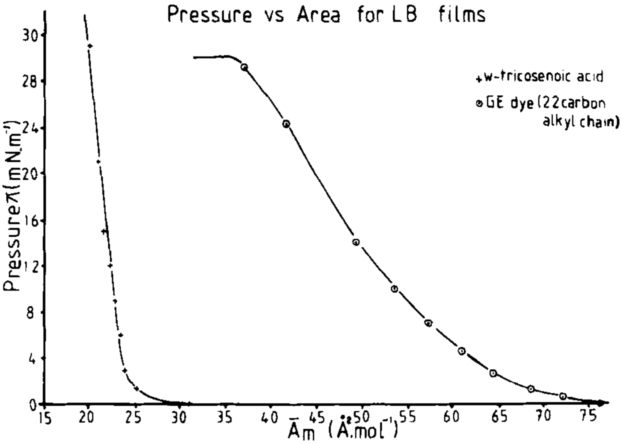


FIGURE 6 Pressure/area isotherms for ω-tricosenoic acid and merocyanine dye samples.

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