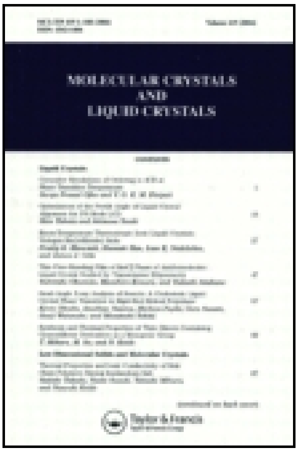

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ON THE STRUCTURE OF MIXED LANGMUIR-BLODGETT FILMS OF TWO DIFFERENT FATTY ACID SALTS

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Abstract Langmuir-Blodgett films of mixed behenic and stearic acid salts of cadmium were deposited and investigated by small-angle X-ray scattering. The ratio of compounds was varied from 1:4 to 4:1. It was found that for 1:1 ratio the lattice spacing was equal to 54.0 Å, which corresponds to double chain length of arachidic acid or to a sum of one chain length of stearic and behenic acid salts. In this case a single completely mixed phase was obtained. For the other ratio X-ray patterns contained two systems of reflections, each of them corresponding to one of the pure fatty acid salts (49.0 Å and 58.5 Å respectively), implying the coexistence of two phases.

Keywords: Langmuir-Blodgett films, structure diffraction

INTRODUCTION

It seems to be important to study the structure of Langmuir-Blodgett films formed by mixing of two different compounds. Fatty acids are often used as an added substance for stabilisation of unstable monolayers (usually of biological objects). The main question is: do the compounds really mix or they form unmixed domains? It seems to be right to begin such a study with a mixture of two simple compounds such as fatty acid salts.

It was already shown by X-ray method [1] that it is possible to mix palmitic and arachidic acids. When the ratio of compounds was equal to unity the spacing of the system was equal to stearic acid spacing (medium spacing of this two acids). Here we report data about the mixture of other acid salts and for these acids we have found coexistence of two phases corresponding to pure acids salts.

MATERIALS AND METHODS

Solutions of stearic ($C_{18}H_{36}O_2$) and behenic ($C_{22}H_{44}O_2$) acids in benzene at the same molar concentration (1M) were prepared.

Mixtures of the two fatty acids in different molar ratios, from 1:4 to 4:1, were used as spreading solutions. The mixing was carried out both by direct dropping of two solutions on the water surface or by mixing them previously in a glass.

Tridistillated water containing 10^{-3} M $CdCl_2$ was used as a subphase (pH 7.2).

Silicon slides with sizes 0.25mm x 5mm x 10mm were used as substrates for LB films deposition. Their hydrophobization was carried out in HF (hydrofluoric acid) by removing an oxide layer. Deposition was carried out just after this treatment.

Monolayers were prepared using a Joyce Loebl Langmuir trough, with two movable barriers, compressing the layers till reaching the surface pressure of 27.5 mN/m, optimal for deposition of fatty acid salts [2].

Films were deposited with the usual Langmuir-Blodgett technique. Each film contained at least 15 periods (30 monolayers) along a normal to the substrate.

X-ray diffraction patterns were obtained by an automatical small-angle X-ray diffractometer with a position sensitive detector [3], using a Nickel filtered CuKα radiation of =1.54 Å. The X-ray beam is collimated with 3 slits and has a width of about 0.05°.

In order to diminish the background scattering the path between the sample and the detector was under vacuum.

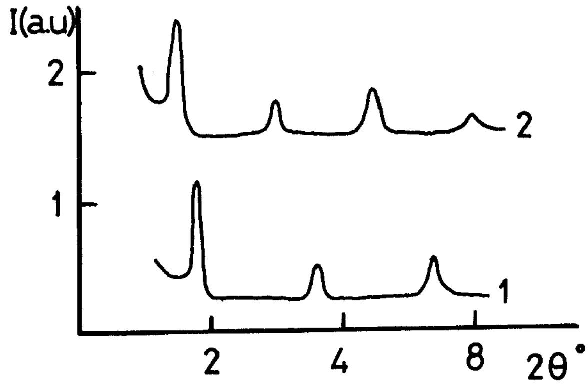

FIGURE 1. X-ray patterns of samples containing 30 monolayers of Cd stearate (1) and 30 monolayers of Cd behenate (2).

The linear resolution of the detector was 0.12 mm; the angular position of peaks was determined with an accuracy of 0.02°.

RESULTS

Diffraction patterns of pure stearic and pure behenic acids salts LB films are shown in FIGURE 1 . These patterns show the presence of a lamellar phase and from the angular position of the peaks it is possible to determine periods of the structures in the normal direction to the bilayer plane.

These periods are d=49.0±0.1 Å for the stearic acid and d=58.5±0.1 Å for the behenic acid salts, both corresponding to the double chain length of the two molecules. The long range order in the stacking of bilayers was also determined from the angular widths of the peaks. It was found that up to 100 layers the long range order approximately corresponds to the total thickness of the sample.

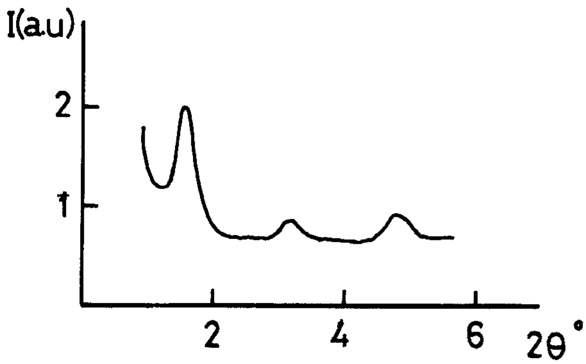

FIGURE 2. X-ray pattern of LB film (30 monolayers) made from previously mixed in a solution of behenic and stearic acids with a molar ratio 1:1.

X-ray pattern of a film formed by using the 1:1 molar ratio mixture is shown in FIGURE 2. The sample was prepared by mixing the two fatty acids solutions before spreading. A single phase is still present and the period is d = 54.0 ± 0.1 Å, which corresponds to double chain length of $C_{20}H_{40}O_2$ (arachidic acid) or to a sum of one chain lengths of stearic and behenic acid salts.

In any other case, that is to say with any other molar ratio mixtures and even with 1:1 molar ratio but if the mixture was obtained not before spreading but by dropping continuously the two solutions directly to the water surface, the resulting X-ray patterns are like the one shown in FIGURE 3.

It is evident from the FIGURE 3 that the diffraction patterns contains Bragg peaks referring to two different coexisting phases, the period of the first one corresponding to that of pure stearic acid, and of the second to that of pure behenic acid salt film.

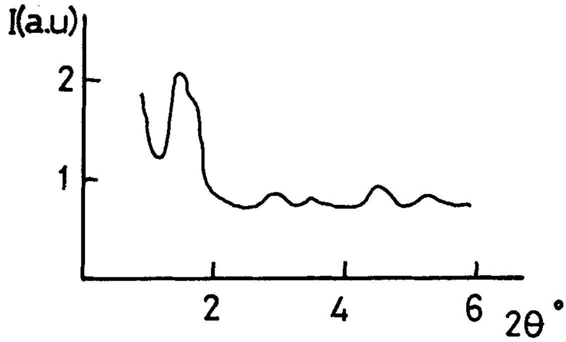

FIGURE 3. X-ray pattern of LB film made from a mixture of behenic and stearic acids at a molar ratio 2:1.

On the basis of the obtained data we can propose the following model of the film formation. At the water surface the molecules of each compound form two-dimensional domains. Such domains are growing even without compression.

According to H.Khun, Langmuir-Blodgett technique is analogous to an epitaxy process, so a previous monolayer is a matrix for the latter, and domains of one compound tend to be near those in the underlayer [4]. So when the amount of one compound is small (up to 10%) we see the X-ray diagram corresponding to the other acid because this compound can be considered as an impurity.

When the amounts of both compounds are comparable (but not equal) we can see two systems of reflections in the X-ray diagram. The molecules of two acids form domains not mixing with each other. This domains grow as monolayers are deposited.

When the ratio is 1:1 and the compounds are mixed in a solution we have only one system of reflections in a X-ray diagram. Such a situation can be due to the fact, that molecules, been mixed in the solution, form mixed domains at the water surface. A domain formation process is equal to a two-dimensional crystallisation. In this case the molecules are similar to each other (the only difference is in the length of hydrocarbon chains) and this is suitable for growing of mixed two-dimensional crystals (domains). The possible packing of molecules in such films is presented in FIGURE 4.

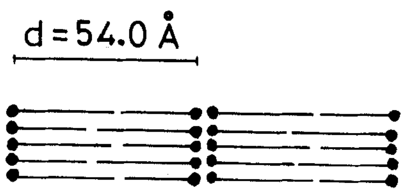

FIGURE 4. Probable packing of molecules of behenic and stearic acids in LB film when the molar ratio is 1:1.

CONCLUSION

To mix two different substances in the same monolayer is a very difficult task even for such simplest compounds like fatty acid salts. A completely mixed sample was obtained only when the molar ratio of two fatty acids was 1:1 and the mixture was done before spreading the monolayer. In all other cases a coexistence of two different phases was observed. So it should be taken into account, that if there is no direct proof, an adding of fatty acid to a monolayer for stabilisation results only in stabilisation of fatty acid domains without a positive effect to the domains of the second compound.

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REFERENCES

1. A.Matsuda, M.Sugi T.Fukui, S.Izima, M.Miyahara and Y.Otsubo, J.Appl.Phys., 48, 771 (1977).
2. G.G.Roberts, Adv. in Phys., 34, 475 (1985).
3. L.Yu.Mogilevsky, A.T.Dembo, Studia Biophysica, 97, 147, (1983).
4. H.Kuhn, J.Photochem., 10, 111 (1979).