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X-ray diffraction technique have been used extensively in order to determine the structural properties of Langmuir-Blodgett films. In this work we employed this technique to investigate the structure of mixed LB films, starting from very simple mixtures (i.e., mixture of long-chain fatty acid salts) to more complicated ones, containing protein fragments. The obtained results show a variety of behaviours and demonstrate that different molecular packing are possible, even in the same molecular system, in connection with small changes in the experimental conditions. In particular it appeared that a real mixing of the two types of molecules involved is not always possible.

INTRODUCTION

The increasing interest of a wide range of specialists about the Langmuir-Blodgett (LB) technique is due to the fact that this method allows one to form structures with molecular alternation of layers.[1] It was already shown by X-ray studies[2] that, by this method, it is possible to organize the so-called LB superlattices (complicated structures with the desirable layer alternation). Furthermore, it was shown by optical methods[3] that the energy transferring between the layers is possible if the structure is organized in a suitable manner.

The experiments indicate the fact that LB technique allows one to realize the molecular architecture (desirable monolayers alternation with fixed distances and mutual orientation of the functioning groups) in the direction normal to the film plane. If one knows the spacings and the molecular orientations in two different layers, he can predict the spacing and the molecular orientation in the LB film built up by successive depositions of the layers.[2] This is due to the fact that the layers are rather "independent" and the contact between layers takes place, for instance for fatty acid LB, in the hydrocarbon chains that are similar to one another.

So the deposition process can be considered as an epitaxial process, where hydrocarbon chains of one layer are a suitable matrix for the next layer deposition.

A different situation seems to appear when two different molecular components are mixed in a single monolayer. Besides being of fundamental interest, the investigation of mixed monolayers is extremely important because of their wide applications. Often scientists use some simple surfactant molecules to fulfill the empty space in the monolayer when working with more complicated molecules for LB depositions.[4]

In other cases it could be necessary to have functional molecules distributed in some manner (not closely packed) in the monolayer. For this purpose usually a mixture of two components (one is a functional molecule and the other one a simple surfactant such as a fatty acid) is used as spreading solution for the monolayer formation. Such an approach is often applied too, while working with protein monolayers.[5] The surfactant molecules in this case are considered to be distributed between the protein molecules.

Do the molecules form a real homogeneous mixture if more than one compound is used for the monolayer formation? A direct answer to this question seems not to be very easy. Fluorescence microscopy technique, widely used for the study of the domain structure of the monolayer, is based, for example, on the fact that the dye molecules cannot penetrate the regions of closely packed hydrocarbon chains.[6] This fact results in the localization of the dye molecules in the areas between the "solid" domains and visualization of the film structure. The aim of the present study was the investigation of several two-compound mixtures, starting from very simple systems to more complicated ones, containing biological molecules.

MATERIALS AND METHODS

Fatty acids (palmitic, stearic and behenic) and the aliphatic amine octadecylamine were purchased from Sigma and recrystallized. The spreading solution contained 0.5–2.0 mg/ml of the surfactants in chloroform.

Langmuir-Blodgett films were prepared on a Joyce Loebl Langmuir Trough. Pure water with the addition of 10^{-4} M of $CdCl_2$ or $Pb(NO_3)_2$ was used as subphase in the case of the deposition of LB films from the mixture of the two fatty acids. Pure water was used as subphase when the mixture of the fatty acid with octadecylamine was spread (tridistilled water from a quartz distilling system).

The compound mixture was done both by mixing in a solution before the spreading and by mixing the compounds in the monolayer at the water surface by successive dropping of the monocompound solutions. Films were transferred onto the hydrophobizated surfaces on silicon substrates by vertical lift technique at a surface pressure of 30 mN/m. Each sample for the X-ray analysis contained 30 monolayers.

X-ray measurements were carried out on a small-angle X-ray diffractometer equipped with a position-sensitive detector.[7] The samples were rotated slowly with respect to the X-ray beam and the diffraction pattern was registered by a position-sensitive detector.

RESULTS AND DISCUSSION

At the beginning, fatty acid salts were considered as mixed compounds because of the similarity of their molecules, in order to realize an ideal model situation. X-ray analysis revealed that different metal atoms in the head groups of molecules (adding Ba or Cd salts into the volume of the water subphase) do not change the spacing and the type of molecular packing in the LB films.

In the case of behenic and stearic acids mixture, the molecular ratios were varied from 1:4 to 4:1. Only in one case, namely when the molecular ratio was 1:1 and the compounds were mixed in a solution before spreading, a single system of reflections was registered at the X-ray analysis (Figure 1). This fact indicates that a film with only one type of structure was created. The value of the spacing in this case was found to be equal to $D = 54.0 \pm 0.5$ Å. The elementary unit in the direction perpendicular to the film plane contains one stearic acid molecule and one behenic acid molecule.

The model of the molecular packing for this LB film is presented in the inset of Figure 1. The value of the spacing is an average between the value of the spacings of LB films of the two pure fatty acid salts, mixed in the solution ($D_1 = 49.0 \pm 0.5$ Å for the stearic acid salt and $D_2 = 59.0 \pm 0.5$ Å for the behenic acid salts,[8] i.e., equal to the sum of the chain lengths of the two fatty acid molecules or to the double chain length of the intermediate fatty acid (arachidic acid).

For all the other molecular ratios and even for the same ratio but mixed at the water surface (by successive dropping of each of the fatty acid solutions at the air/water interface) the formation of the LB films occurred whose X-ray patterns contained two different systems of reflections. It means that regions with two

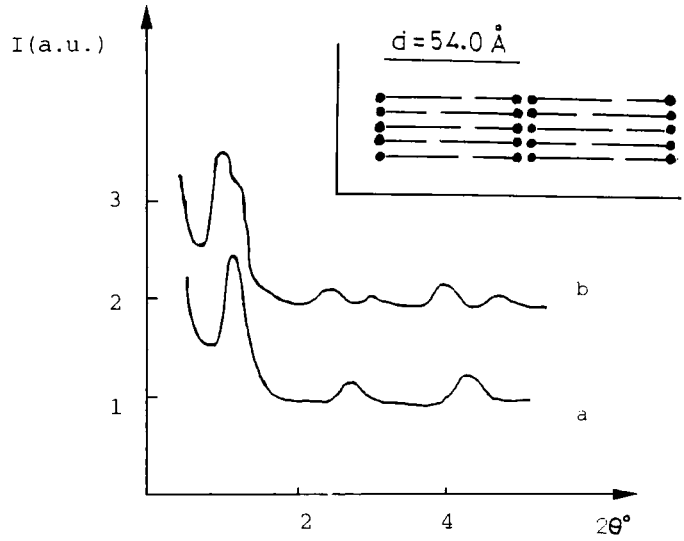

FIGURE 1 X-ray diffraction pattern of LB films of mixed stearic and behenic acid salts with a molar ratio 1:1 (a) and with a molar ratio different from 1:1 (b). In the inset the probable molecular packing at a molar ratio 1:1 is shown: the longest molecules are those of behenic acid salts, the shortest those of stearic acid salts.

different molecular packings were coexisting in the LB film. The spacings resulted to be, respectively, $D_1 = 49.0 \pm 0.5$ Å and $D_2 = 59.0 \pm 0.5$ Å, that are equal to the spacings of LB films of pure stearic and behenic acid salts.

On the basis of this result, it was natural to expect that considering two other different fatty acids a similar behaviour would have been observed. For this purpose we investigated a new system, consisting in a mixture of palmitic and behenic acids. The two acids were mixed before spreading on the trough. The typical diffraction patterns obtained from Langmuir-Blodgett films of mixed palmitic and behenic acid salts are shown in Figure 2. The main difference with the previous system is that in this case a single phase is present for any molar ratio of compounds; the lattice spacing changes by steps, going from a minimum of $D = 50.0 \pm 0.5$ Å to a maximum of $D = 60.0 \pm 0.5$ Å, as shown in Figure 3.

When the molar ratio is 1:1 the spacing corresponds to the double chain length of the intermediate fatty acid. For molar ratio different from 1:1 the spacing varies not continuously with respect to the concentration of compounds, resulting in at least five different molecular packing arrangements, as can be seen in the step function of Figure 3.

Moreover the Scherrer equation

$$D = \frac{K\lambda}{\beta \cos \theta} \tag{1}$$

(where K is a constant approximately equal to 1, β is the angular width at half-

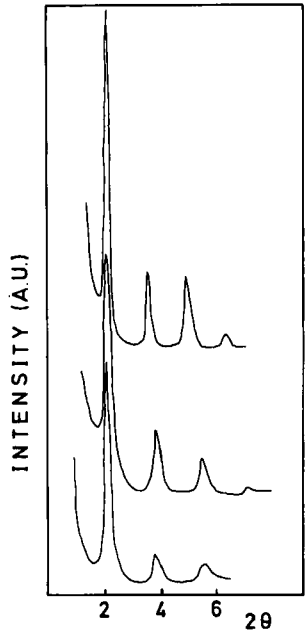

FIGURE 2 X-ray diffraction patterns of LB films of mixed palmitic and behenic acid salts with molar ratio 1:2 (a), 4:1 (b), 8:1 (c), respectively.

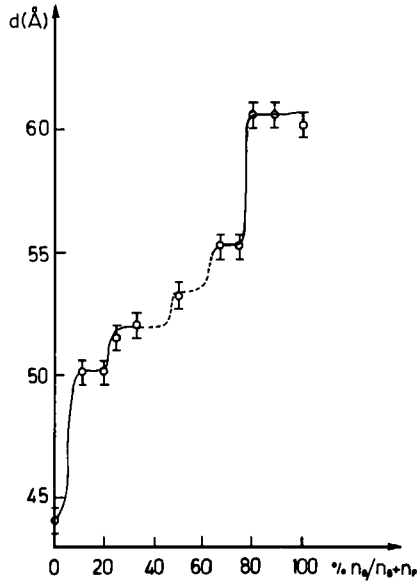

FIGURE 3 Plot of the lattice spacing of LB films of mixed behenic and palmitic acid salts versus behenic acid molar concentration.

maximum intensity of a Bragg peak and θ the angle of its corresponding reflection), was used to determine the lower limit of the correlation length D_{min} in the direction perpendicular to the films (i.e., approximately the thickness of the sample over which the unidimensional periodic arrangement extends). In fact in Equation (1) the measured width β was inserted, thus providing the lower limit of D, for the exact determination of which a precise knowledge of the experimental resolution function would have been necessary.

The results of β and D_{min} are reported in Table I, together with the spacing values. It is observed that for LB films of pure fatty acid salts, the lower limit of the correlation length corresponds to 8–10 bilayers, a value comparable to the total number of deposited bilayers. For all the examined mixtures of stearic and behenic acid salts, the D_{min} value is lower and corresponds to 4–5 bilayers; finally, for the mixtures of behenic and palmitic acid salts D_{min} does not wander off the value obtained in the case of pure compounds and corresponds to 6 bilayers at least.

In conclusion it appears that once a segregation of domains of the two different molecules occurs in a given layer this information is transmitted to the following layers if not for all the thickness of the LB films at least for a thickness of the same order of magnitude. That suggests that, when phase separation is observed, a selective diffusion process occurs at the air-water interface, involving the monolayer molecules during the deposition process, in order that each one of the two types of molecules is able to deposit on a similar molecule. This fact suggests that the in-plane size of domains cannot be very large. A schematization of domains formation is shown in Figure 4. It is foreseen to carry out in the near future atomic force microscopy observation of the two types of domains in our LB films, as this

TABLE I

Lattice spacing, half-maximum width and lower limit of the correlation length for the different examined samples

Sample	d(Å)	β(°)	D_{min}(Å)
Stearic Acid	49.0±0.5	0.16	484±50
Behenic acid	58.5±0.5	0.26	360±40
Stearic Acid/ Behenic Acid 1:1	54.0±0.5	0.41	215±20
Stearic Acid/ Behenic Acid 2:1	49.0±0.5 58.5±0.5	0.40 0.40	220±20 220±20
Stearic Acid/ Behenic Acid 1:2	49.0±0.5 58.5±0.5	0.40 0.40	220±20 220±20
Palmitic Acid	43.0±0.5	0.19	464±50
Behenic acid	58.5±0.5	0.26	360±40
Palmitic Acid/ Behenic Acid 1:1	53.1±0.5	0.24	367±30
Palmitic Acid/ Behenic Acid 4:1	50.0±0.5	0.31	285±20
Palmitic Acid/ Behenic Acid 1:8	60.4±0.5	0.24	370±30
Stearic Acid/ Octadecylamine 1:1	52.0±0.5	0.12	735±70

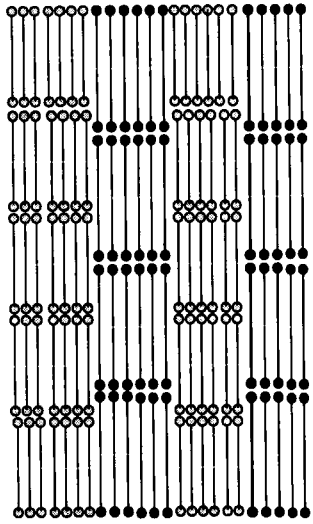

FIGURE 4 Schematization of the molecular packing of mixed LB films of behenic and stearic acid salts with molar ratio different from 1:1.

technique was used very recently[10] to directly image and differentiate chemically domains in phase-separated films of molecular mixtures, probing their material properties down to the atomic scale.

Another investigation was done using different kinds of molecules, namely a fatty acid and an aliphatic amine. In particular we used a mixture of stearic acid and octadecylamine (the lengths of their hydrocarbon chain are the same). Pure

distilled water was used as subphase in this case. The same approach used in the previous investigation involving fatty acid salts only was utilized. First, monolayers containing the two compounds with different molar ratios were spread, then LB films were deposited and analyzed by X-ray diffraction.

Good mixing of the compounds, with high ordering was observed when the molar ratio was 1:1. The corresponding X-ray diffraction pattern is presented in Figure 5. The pattern contains 5 orders of reflection. The spacing was found to be D = 52 ± 0.5 Å, and the packing of molecules is shown in Figure 6: the unit cell is formed by the two different molecules, but unlike these from the case of the two fatty acids, these molecules have the same length and different head groups.

It is natural to suppose, that each stearic acid molecule is in contact with an octadecyalmine one in adjacent layers; their interaction has an electrostatic origin since, at a neutral pH, stearic acid head groups have a negative charge while octadecylamine has a positive charge.

It should be also mentioned that the mixed film in this case is very well-ordered. The lower limit of correlation length calculated from the half width of the reflection was found to be D_{min} = 735 ± 50 Å (the length ordering). The total thickness of the film, containing 30 monolayers is 770 Å. Thus we can say that all our film in this case is inside the range of ordering.

The X-ray diffraction pattern shows also a small peak at $2\theta = 3.1°$. It can be explained as a second order reflection of the system, giving the spacing D = 56.0

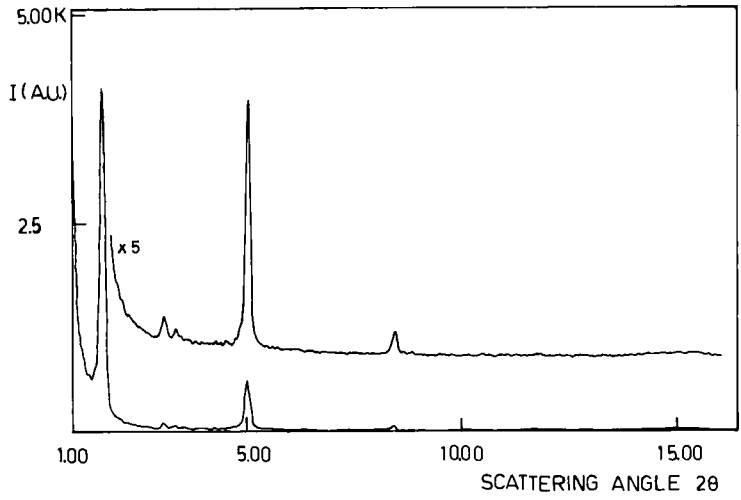

FIGURE 5 X-ray diffraction pattern of LB films of stearic acid and octadecylamine with molar ratio 1:1.

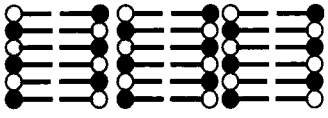

FIGURE 6 Model of the molecular packing of LB films of stearic acid and octadecylamine. The unit cell contains a molecule of each of the two compounds.

Å and it seems to be associated to another phase. As the amount of this phase, calculated by taking integral reflections for both phases, is small (less than 2%) it can be attributed to a lamellar structure, formed by impurity molecules, differing from the main one by an increased chain length. Investigation was then extended to samples containing stearic acid and octadecylamine in different molar ratios. In particular molar ratio 2:1 and 1:2 were taken into account. Monolayers deposition turned out to be worse in these conditions than in the case when the molar ratio was 1:1, as it was shown by a transfer ratio much less than 1. A single system of reflections was present in the diffraction pattern when the ratio octadecylamine/stearic acid was 2:1 giving a spacing lattice $D = 52.0 \pm 0.5$ Å, exactly corresponding to that obtained with molar ratio 1:1 (Figure 7).

A different experimental result was obtained when stearic acid was present in larger amount than octadecylamine (molar ratio octadecylamine/stearic acid 1:2). In this case in fact, two systems of reflection were obtained; in addition to the lamellar system with $D = 52 \pm 0.5$ Å, a second system appeared, corresponding to pure stearic acid (Figure 8). This fact indicates that there is a segregation of

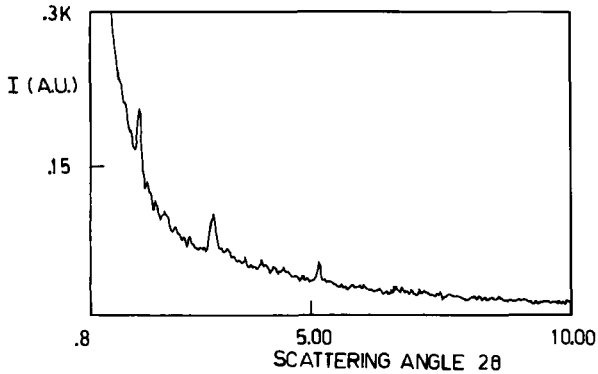

FIGURE 7 X-ray diffraction pattern of LB films of stearic acid and octadecylamine with molar ratio 1:2.

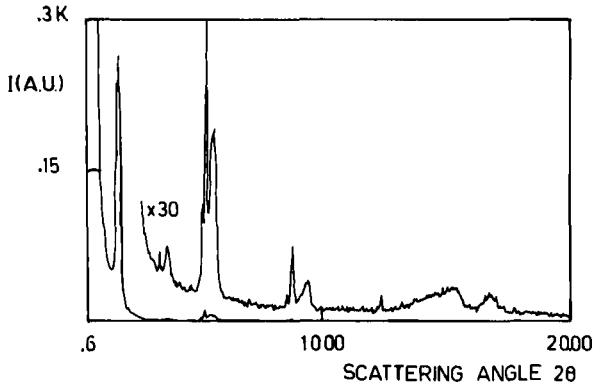

FIGURE 8 X-ray diffraction pattern of LB films of stearic acid and octadecylamine with molar ratio 2:1. It is possible to observe two systems of reflections.

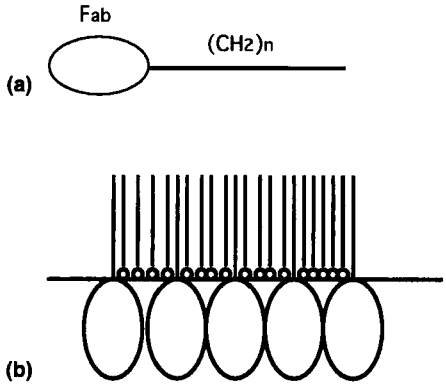

FIGURE 9 (a) Schematic representation of a Fab fragment. Polar head and hydrophobic chain are drawn in right proportion. (b) Monolayer of a Fab fragment with stearic acid molecules filling empties between proteins.

pure stearic acid with respect to homogeneous mixture. Therefore the behaviour of these systems is still different as compared to the several ones observed in the case of fatty acid salts mixtures.

Finally a fourth investigation of mixed system, was done with one of the most complicated objects: proteins.

Hydrophobizated Fab fragment of an antibody (immunoglobuline G) was used for the LB film formation.[9] The formula of the component was the following:

$$Fab—S—S—(CH_2)_2—CO—NH—(CH_2)_{15}—CH_3$$

The LB film of this component deposited onto a solid substrate doesn't show a good ordering. In order to make the film more ordered the following attempt was undertaken. Mixed monolayer, containing this compound and stearic acid (or octadecylamine) in the molecular ratio corresponding to the close packing of Fab fragment under the water and close packing of hydrocarbon chain in the air (Figure 9), was spread at the air/water interface. As sizes of Fab fragment differ dramatically from hydrocarbon chain sizes, we added such amount of stearic acid, necessary to fill all empties. The film was deposited onto a solid substrate and X-ray scattering measurement revealed that the desirable packing was not obtained. The most probable explanation of this fact consists in the formation of different not mixed domains of the two compounds. Further attempt will be carried out in the near future to improve the situation.

CONCLUSION

The conclusion of the present work is that a prediction of final structure of LB films, whose monolayers contain only two different types of molecules is a very

complicated task. In fact even for simple molecules we obtained different results after variation of hydrocarbon chains by only two carbon atoms. In particular we obtained that the mixture of stearic and behenic acid salts gave rise to a really mixed system only when the molar ratio of the two compounds was 1:1; for any other molar ratio mixture, a coexistence of phase was observed, corresponding to domains of the two single compounds. On the contrary, LB films deposited with the mixture of palmitic and behenic acid salts contained, at any investigated molar ratio, a single phase, but with variable lattice spacing, depending on molar ratio of the two compounds. The mixture of stearic acid and octadecylamine gave rise to a single system of reflections, corresponding to $D = 52.0 \pm 0.5$ Å, but when stearic acid was present in larger amounts than the aliphatic amine, it originated a separate phase.

Anyhow the complexity of the phenomena observed suggests that further investigations are necessary in order to better understand the physical properties of mixed LB films: in particular atomic force microscopy should complement the X-ray diffraction work. The results point out that in all experiments when one type of molecule is used in order to stabilize or to separate molecules from the others, experiments should be done "a priori" proving the real mixing of compounds.

In the case of more complicated systems, the situation is even worse because it is very difficult to deposit a lamellar structure, ordered enough for investigation with X-ray methods.

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