ESRF	**Experiment title: RELAXATION IN TWO-DIMENSIONAL MICROEMULSIONS**	**Experiment number**: SC 827
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Names and affiliations of applicants (* indicates experimentalists):

F. Perrot*[1], S. Cantin*[1], V. Dupres*[1], F. Benhabib [1], J. Daillant [2], P. Fontaine*[2]

[1] Laboratoire de Physique des Matériaux et des Surfaces,
Université de Cergy-Pontoise, Neuville sur Oise,
F-95 031 Cergy-Pontoise cedex (France)

[2] LURE, Centre Universitaire Paris Sud, BP 34,
F-91898 Orsay cedex (France)

Report:

In order to study the structural relaxation of the two-dimensional microemulsion of stearic acid-FEP mixtures, we used Grazing Incidence X ray Diffraction. The angle of incidence of the X-ray beam was fixed to 0.85 α_c, where α_c is the critical angle for total internal reflection. The wavelength was fixed to $\lambda = 1.552$ Å . The Langmuir trough, mounted on a vibration isolation system and used at room temperature (20°C), was equipped with a single barrier for the monolayer compression and with a Wilhelmy balance for the surface pressure control. The volume of the trough was 0.4 l. The diffracted intensity was recorded by a vertical gas-filled position sensitive detector (PSD). The measurement of the intensity as a function of the in-plane component Q_{xy} of the scattering vector, integrated over the vertical component, Q_z, yields Bragg peaks. The Q_{xy} resolution provided by a Soller collimator in front of the PSD was 0.007 Å^{-1}. From the Q_{xy} position of the peaks, the parameters of the unit cell can be deduced. By extracting the Q_z dependence of the intensity across each Bragg peak (Bragg rod profiles), the tilt direction and the tilt angle can be determined.

Different parameters have been varied : surface pressure, length of the fatty acid (behenic acid), Cd^{++} ions in the subphase (pH 6.5). Erratic results have been obtained. Nevertheless, surstructures have been observed at room temperature at zero pressure with microemulsions containing behenic acid with Cd^{++} ions in the subphase at concentration of 10^{-5} mol/l.

So, we decided to perform systematic experiments on behenic acid (BA) monolayers with cadmium chloride in the subphase at zero pressure.

Over a cadmium concentration range $2.5.10^{-6}$ to 10^{-4} mol/l, a superlattice structure corresponding to an organized layer of cadmium ions or cadmium hydroxide complex is evidenced (see fig 1). Contrary to arachidic acid and heneicosanoic acid monolayers spread over concentrated cadmium subphases, that display surstructures only at low temperature, a superlattice structure is evidenced at ambient temperature in BA monolayers. Compared to results obtained on arachidic acid and heneicosanoic acid monolayers, the superlattice parameters and the fatty acid parameters remain the same. The fatty acid chain length does not seem to play a role in the superlattice formation.

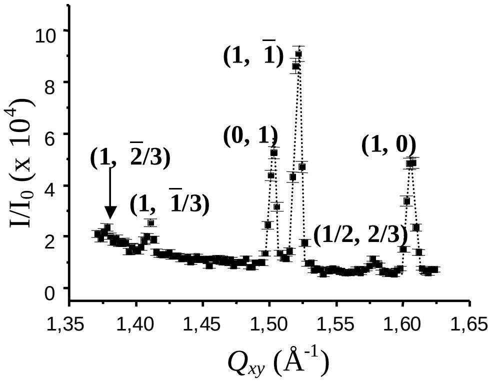

Fig. 1 : X-ray diffraction data in the horizontal plane, integrated over Q_z for a behenic acidd Langmuir monolayer on a cadmium chloride (10^{-4} mol/l) at room temperature and at zero pressure. The peak index correspond to the unit cell with one molecule.
The presence of three peaks indicates an oblique unit cell with dimensions *a'* = 4.59 Å , *b'* = 4.90 Å and γ' = 121.6°, corresponding to an equivalent pseudo-rectangular unit cell with lattice parameters *a* = 4.59 Å, *b* = 8.38 Å and γ = 93.7°. The tilt angle is about 9.5°.

Moreover, we have observed a degradation of the films as a function of time, which was all the more fast as the $CdCl_2$ concentration increases.

At a cadmium chloride concentration of 1.9 10^{-6} mol/l, the superlattice structure is no longer detected. For this concentration, the sequence of phases is the same as that obtained over pure water (see fig.2). The transition L_2 -L'_2 is found at the pressure of 14 mN/m instead of 20 mN/m on pure water and the transition L'_2 – S occurs at 26 mN/m instead of 32 mN/m on pure water. The phase transitions occur at lower surface pressure and the tilt angle of the molecular chains is lower, indicating the condensing effect of the divalent cations.

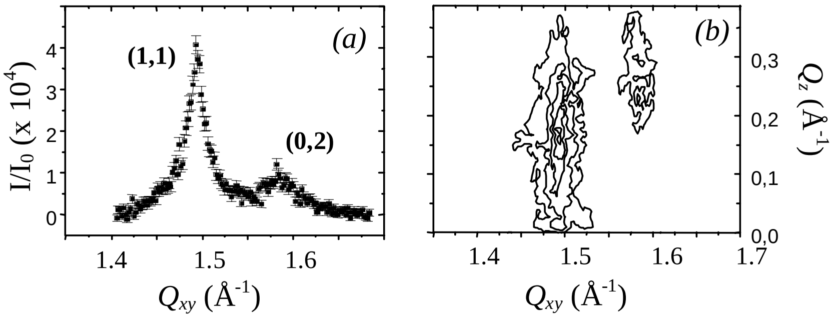

Fig. 2 : X-ray diffraction data in the horizontal plane, integrated over Q_z (a) and contours of equal intensity vs the in-plane and out-of-plane scattering vector components Q_{xy} and Q_z (b) for a behenic acid Langmuir monolayer on a cadmium chloride (1.9 10^{-6} mol/l) at room temperature and at pressure 20 mN/m. The peak index correspond to the unit cell with two molecules. The diffraction pattern corresponds to a L'_2 phase. In the rectangular unit cell, the lattice parameters are *a* = 4.96 Å, *b* = 7.87 Å. The tilt angle is 10°.

The existence of a threshold of cadmium concentration is demonstrated for the superlattice formation. In order to have a better understanding of the phenomena, we use for the cadmium chloride concentration a better unit, which is the number of cadmium ion per BA molecule. Indeed, for $CdCl_2$ concentrations corresponding to more than 2.5 cadmium ions per BA molecule and higher, one obtains a superlattice structure similar to that previously reported in arachidic acid and heneicosanic acid monolayers. In other words, at least two layers of ions are necessary to form a superlattice. Below the threshold, these results indicate that the addition of a very low quantity of cadmium ions (around 10^{-6} mol/l) in the subphase of fatty acid monolayers is sufficient to obtain more condensed phases, which can be of interest for LB transfer.

Study of the observed superlattice by grazing-incidence surface scattering can allow a better understanding of this effect.

These results are presented in a manuscript submitted to *Eur. Phys. J. E.*