

**Experiment title:** STRUCTURE AND FLUCTUATIONS OF LIQUID SURFACES : MONOLAYERS AND ELECTROLYTES.

**Experiment number:**  
SC-688

**Beamline:**  
ID10 B

**Date of Experiment:**  
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**Shifts:**  
18

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*Received at ESRF:*

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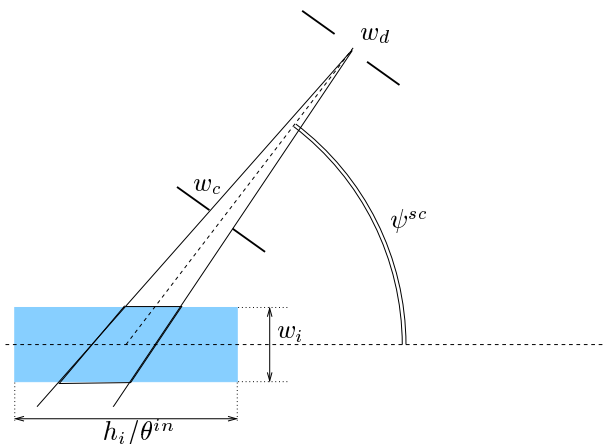
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**Report:**

This experiment was the final part of the long term project "Structure and fluctuations of liquid surfaces", SC-688. The aim of the experiment was to investigate the effects of ions at liquid interfaces. We studied simple 1:1 electrolytes and the effect of divalent cations on a monolayer.

- The experimental setup was quite similar to those of the previous experiments (SC-441 and SC688 for instance). The experiment consists in measuring the diffuse intensity scattered by the surface with an incidence below the critical angle for total external reflection. The detector was a vertically mounted gas-filled position sensitive detector (PSD), and the energy was fixed to 8 keV. Diffuse intensity roughly scales with  $q^2$ ,  $q$  being the wave-vector transfert.



**Fig.1-** The vertical  $\times$  horizontal dimensions of the detector slit  $S_d$  and of the slit placed just after the sample  $S_c$  are  $(h_d \times w_d)$  and  $(h_c \times w_c)$ . The dimensions of the slit placed just before the sample  $S_i$  are  $(h_i \times w_i)$ .  $\theta^{in}$  is the angle of incidence. Total illuminated area (fig.1, in grey) is  $h_i \times w_i / \theta^{in}$ , but the effective illuminated area is lower (roughly proportional to  $w_c$ ). Detector's solid angle is proportional to  $w_d$ . So, intensity collected in the detector is proportional to  $w_c \times w_d$ .

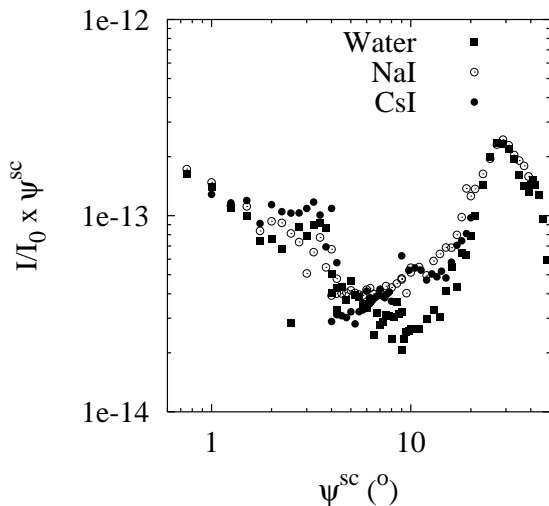
Since we were interested in very large wave-vectors transfer ( $q = 10^9 - 10^{10} m^{-1}$ ), we modified the setup by using quite large slits ( $w_c=1000 \mu m$  and  $w_d=3000 \mu m$  instead of  $w_c=300 \mu m$  and  $w_d=500 \mu m$ , see fig.1), so that the detector solid angle and the effective illuminated area were larger than in the previous experiments. Whereas angular resolution is coarser, the scattered intensity is amplified and error bars are dramatically reduced.

- The use of the large slits  $S_c$  and  $S_d$  (fig. 1) was particularly suitable to study surface fluctuation spectra of 1:1 electrolyte surfaces at large  $q$  : to minimize bulk scattering (density fluctuations and ion-ion correlations), the angle of incidence ( $\theta^{in}$ ) must be as small as possible in order to minimize the penetration length of the x-ray radiation. Large slits compensate for the decrease in the cross section due to a small  $\theta^{in}$ .

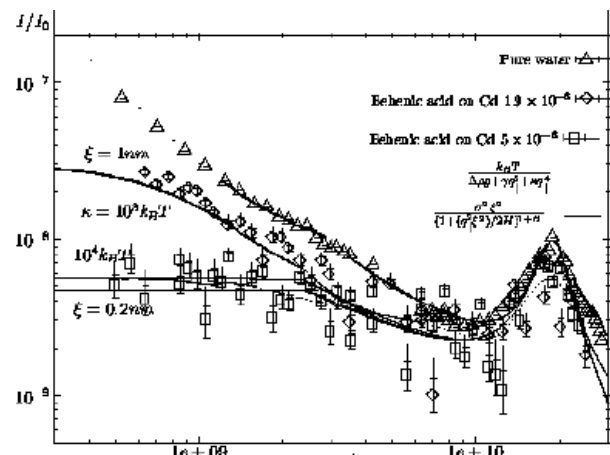
Electrolytes were cesium iodide ( $0.1 \text{ mol.L}^{-1}$ ) and sodium iodide ( $0.1, 10^{-2}$  and  $10^{-3} \text{ mol.L}^{-1}$ ). Two incidences were tested for each sample ( $\theta^{in}=0.98 \text{ mrad}$  and  $2.45 \text{ mrad}$ ) in order to evaluate bulk contributions. Curves we obtained clearly show an excess of the scattered intensity when electrolytes are added (see fig. 2). A detailed analysis is necessary to determine the origin of the excess.

- Above a concentration threshold, certain divalent cations like  $Cd^{2+}$  induce the formation of an inorganic superlattice below fatty acid monolayers. This superlattice is expected to stiffen the monolayer at little scales. This could be an example of a “polymerised membrane”. The monolayer was made of behenic acid with  $Cd^{2+}$  in the bulk, below and above the superlattice formation threshold. In order to control radiation damage, we checked every 15 min that the superlattice peaks were still present. If the test was negative, the monolayer was translated in order to work on a fresh piece of film.

The results are quite encouraging : scattering by the behenic acid/ $Cd^{2+}$  complex monolayer at the air-water interface below and above the threshold for superlattice formation shows that the roughness spectrum is extremely different : to be more precise, the superlattice phase is molecularly flat for wave-vectors larger than  $10^9 m^{-1}$  : there are no capillary waves, contrary to what is observed below the threshold or for other liquid surfaces (see fig.3). Because of the large slits (see above), it was not possible to investigate smaller wave-vectors. We will use a better resolution after solving radiation damage problems in order to have access to smaller wave-vectors and so to have a precise measure of the bending rigidity constant of the surface.



**Fig.2-** Scattering intensity collected in the PSD for water, CsI and NaI,  $0.1 \text{ mol.L}^{-1}$ . The angle  $\psi^{sc}$  is defined in fig.1. Intensity excess with electrolytes may be explained by ion-ion correlations scattering or higher surface fluctuations.



**Fig.3-** Scattering by water and the behenic acid- $Cd^{2+}$  complex monolayer below and above the threshold : capillary waves are suppressed above the threshold, and only molecular roughness remains.