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Short Communications

Photoelectron Spectroscopy of Fatty Acid Multilayers

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A new type of electron spectroscopy for chemical analysis (ESCA) has been developed (*cf.* Refs. 1–3). It employs photo and Auger electrons that are emitted from surfaces exposed to X-radiation. Such electron spectra can now be studied in considerable detail and they contain basic information on the electronic structure of the irradiated specimen. As electrons with energies of several keV or less penetrate only very thin layers of solid matter the method is essentially a surface method. This feature may be of special interest in surface chemistry, and one such application will now be reported. An earlier attempt to use a photoelectron spectroscopy method to the study of built-up films reported by Steinhard and Serfass [4] gave very little information as the sharp electron lines corresponding exactly to the energy of the electron shells [1-3] were not known then.

It is possible to build up multilayers of many long-chain compounds on solid surfaces from monolayers deposited on water.[5-7] The general features of the molecular packing in these layers can be determined by X-ray diffraction methods, and multifilms of, *e.g.*, fatty acids can therefore be used as known models in order to test the capability of physical methods in revealing the molecular packing in phase boundaries. It has furthermore been shown that replacement of methyl groups in long-chain compounds by bromine or iodine atoms does not generally influence the molecular arrangement in the solid state [8] which provides a possibility of "labelling" different parts along a hydrocarbon chain. The result of measurements with the photoelectron method on such "labelled" multilayers will be reported here. An alternative method to study molecular order in surface films of organic substances is low-energy electron diffraction but a serious complication there is the insulating properties of the film.

A monolayer of very pure DL-α-bromostearic acid was spread on water and its pressure was kept constant by a piston of castor oil. The multilayers were built on chromium plated brass slides. Two samples with 200 molecular layers were prepared and two layers of stearic acid were deposited on one of them. The long-spacings of the multifilms were determined by X-ray diffraction using Cu$K\alpha$ radiation. The molecular packing in the surface films according to the X-ray analysis is illustrated in Fig. 1.

The electron spectra of the two samples were recorded in a high resolution spectrometer with two-directional focussing. Photoelectrons expelled by Al$K\alpha$ radiation from the K shell of carbon and the $M_{IV,V}$ shell of bromine were studied. Detection was made by Geiger counter.

No signal from the chromium backing was obtained but well-defined bromine lines were recorded from both samples showing that a film of 8000 Å thickness gives complete shielding whereas atoms covered with about 50 Å of organic material can be

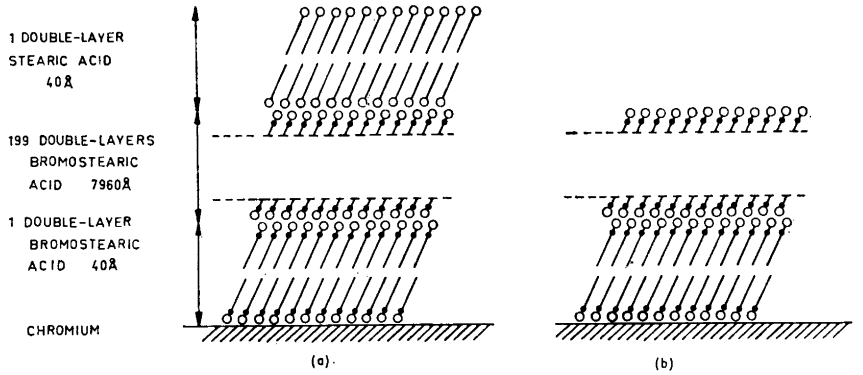

Fig. 1. Illustration of the molecular packing in the multifilms of the two samples where 200 layers of DL-α-bromostearic acid are deposited. Sample (a) is also covered with 2 layers of stearic acid. The axis of the hydrocarbon chain of the molecule is shown, the carboxyl group is indicated by an open circle and the branching bromine atoms by a filled circle.

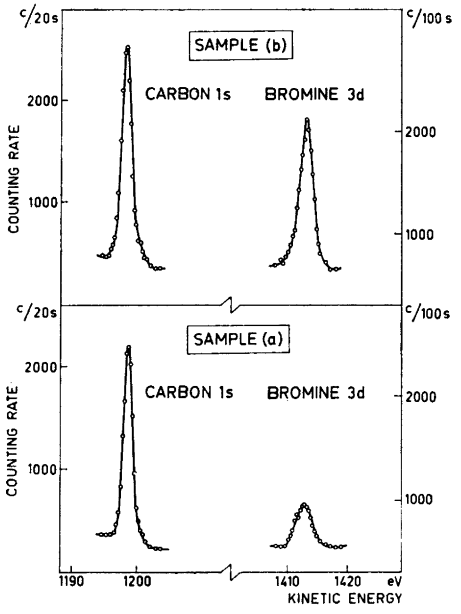

Fig. 2. Photoelectron lines from bromine and carbon in the two samples. The relative intensity of the bromine signal becomes significantly smaller when a double-layer of stearic acid is deposited on top of the multifilm of DL-α-bromostearic acid.

detected by the photoelectron method. The most interesting result, however, was the relative intensities of the bromine and carbon signals from the two samples. As seen in Fig. 2 the intensity of the bromine signal in relation to the carbon signal was significantly smaller for the slide where the α-bromostearic acid was covered with two layers of stearic acid (sample (a)). Electron spectroscopy can therefore be a very useful method for studies of the molecular packing and the occurrence of defects in monomolecular layers.

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