NANOELECTRIC PHENOMENA IN LANGMUIR MONOLAYERS

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SUMMARY
A monolayer of amphiphilic molecules at the air/water interface is studied using the displacement current technique in the metal/air-gap/monolayer configuration. The vertical component of the molecular dipole moment is evaluated during lateral compression. The dielectric relaxation phenomena in the monolayer are investigated in the dependence of the polar orientational order of constituent molecules.

1. INTRODUCTION

As a result of the development of materials science in the "nano" direction, Langmuir-Blodgett (LB) films have been attracting stimulating attention. This interest is fed by the opportunity of forming layered structures by the consecutive deposition of monomolecular layers of various surface-active substances. The structure and physical properties of ultrathin organic layers are fundamentally interesting to the field of physics, chemistry, biology, and electronics. Particularly, the conformation of constituent molecules is essential for the unique properties of the system.

Monolayers formed on the water surface are one of the artificial model systems extensively studied for molecular electronics, because the flat surface of water is an ideal substrate for a further technological treatment in the Langmuir-Blodgett deposition. In addition to that, monolayers on the water surface exhibit interesting physico-chemical properties as literally two-dimensional systems. Much attention is paid to the detection of dynamic behaviour of molecules in a monolayer because purposeful electron transfer or orientational changes in polar molecules is required for the fabrication of a molecular electronic device. From the point of view, the thermally stimulated depolarization (TSD) current flowing across multilayers is very powerful method. Yet, it is very difficult to obtain reproducibility in the TSD experiment, in particular, in the measurement of one-layer films sandwiched between top and base electrodes, principally due to destruction of the film by the application of the top contact.

We introduced a modified version in which the top contact is detached from the upper surface and the Maxwell displacement current (MDC) is detected in the metal/air gap/Langmuir monolayer/metal structure. This strategy can even be used for the study of the dynamic behaviour of monolayers at the air/water interface [2]. MDC flows when the vertical component of the polar molecule changes
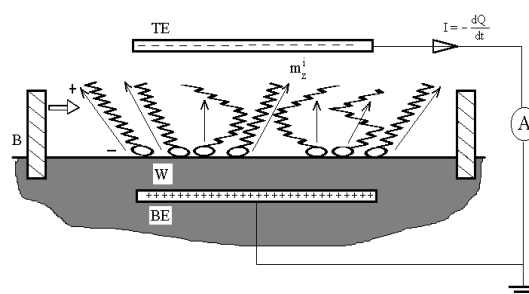
Fig. 1 Experimental setup used for the detection of displacement current in the monomolecular layer on the water surface.

with time. For this reason, the MDC measuring system is suitable for detecting dielectric relaxation phenomena in a monolayer at the air/water interface. In this paper, we discuss the evaluation procedure of the molecular dipole moment and also the dielectric relaxation phenomena accompanying the orientational ordering and disordering of monolayers by applying lateral monolayer compression.

2. EXPERIMENTAL

Fig. 1 shows the experimental setup in this investigation [1]. The top electrode – TE – (the area is S = 20 cm^2) was suspended in air, parallel to the water surface. The air gap between TE and the surface was adjusted to d = 0.5 mm with the aid a micrometer by monitoring the capacitance of the system. The displacement current was detected by a Keithley 517 electrometer (A). The sensitivity of measuring a current was 0.1 fA, the background noise was suppressed by electrical shielding to 2 fA. The measuring system was attached to the computer-controlled Langmuir trough (NIMA Technology, UK) and placed in a dust-free compartment on an antivibrating block.

As a surface-active substance, straight-chain hydrocarbon stearic acid (SA) was used, purchased from

Lachema (Brno, Czech Republic). Stearic acid was dissolved in chloroform (1 mmol/l solution) and slowly added to the surface of bidistilled water (12 MΩcm) to form a single monolayer at the air/water interface. The Langmuir trough was of a rectangular shape with the total working area of 600 cm^2. The compression rates were varied between 20 and 120 cm^2/min, which corresponded to about 0.05 to 0.30 Å^2/s per a molecule.

The displacement current in the circuit originates from three components [2]:

$$I = \frac{N}{d}\frac{dM}{dt} + \frac{M}{d}\frac{dN}{dt} + \frac{\varepsilon_0 S}{d}\frac{d\Phi}{dt} \qquad (1)$$

The first contribution arises from the change in the vertical component of the molecular dipole moment (*M*), the second contribution is connected with the change in number of molecules (*N*) between the electrodes. The third component was taken as zero because the surface potential of water *Φ* may be considered constant during the monolayer compression.

3. RESULTS AND DISCUSSION

A typical recording of the Maxwell displacement current detected simultaneously with the surface pressure (*π*) - area per molecule (A) isotherm during the lateral compression of the monolayer is presented in Fig. 2. The current maximum is located at ca. 0.40 nm^2, which indicates that the rate of ordering process is the highest at the gas-liquid phase transition and the molecules become aligned perpendicularly to the interface. On reversion of the barrier motion, during expansion, the recording almost retraces itself (except the sign), suggesting the reversibility of the process. The area under I – t dependence (integral $\int I(t)dt$) can be utilized for the calculation of the change in the induced charge on electrode 1 and, hence, for the calculation of the molecular dipole moment. The value 2.5x10^{-30} Cm or 750 mD was found for a stearic acid molecule.

As can be seen from the experimental results the signals detected are very low and therefore the problem of background should be carefully considered. The water used in the experiment was bidistilled with subsequent deionization. Therefore, the amount of extrinsic ions was minimized. The effect of intrinsic ion (H$^+$, OH$^-$) motion is negligible because no external potential is applied between the electrodes and furthermore, the air gap between electrode 1 and the water surface is a good electrical insulator and there is no leakage current in the experiment.
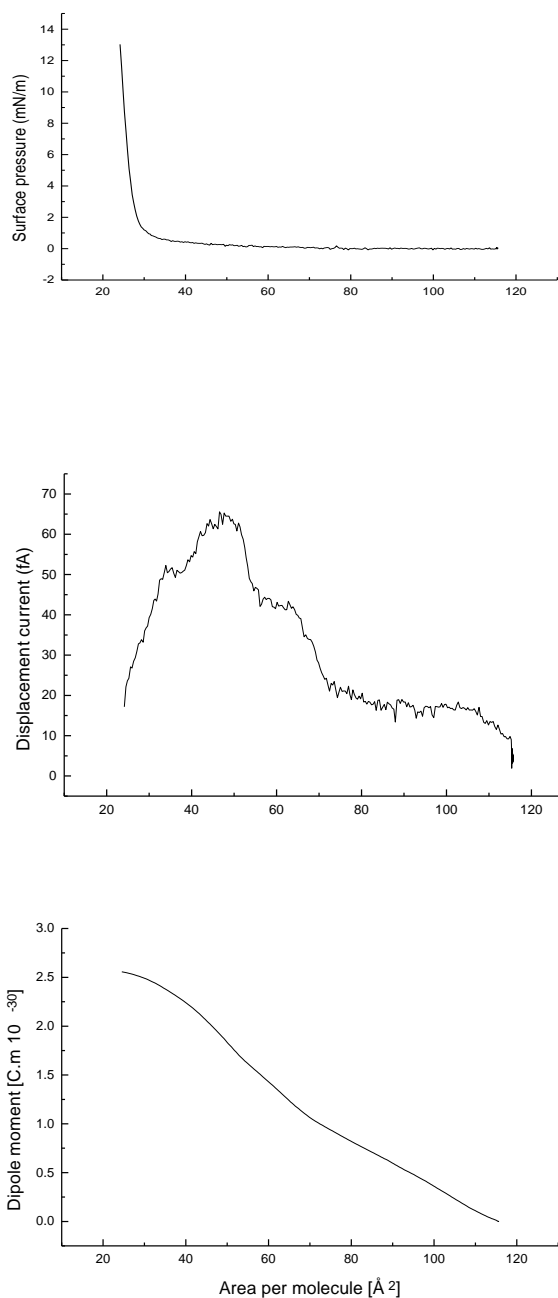

Fig. 2 Surface pressure (π) – area isotherm of SA as recorded together with the displacement current as a function of the area per a molecule. The lower curve shows a calculated molecular dipole moment as varies during the compression

These predictions were always verified by measuring the Maxwell displacement currents on pristine water subphase before spreading the organic monolayer. Under this condition the background signal is at the level of 1 to 3 fA, i.e. more than one order of magnitude below the signal detected with the monolayer. Some other electrical effects (e.g. ionization of the monolayer) might contribute to the induced

charge on the upper electrode. Our detected signal is generated by the change of the induced charge in time and, thus, the above-mentioned effects cannot account for the temporal variations in the charge during the experiment.

The external compression of the monolayer on a water surface with an aid of a movable barrier can be used for studying non-equilibrium phenomena. For this purpose, the motion of the barrier was not continuous but regularly interrupted so as to allow the monolayer to reach an equilibrium state after stopping the barrier. The transient process was monitored by measuring the displacement current across the monolayer. The recording of such a multi-step compression is presented in Fig. 3.
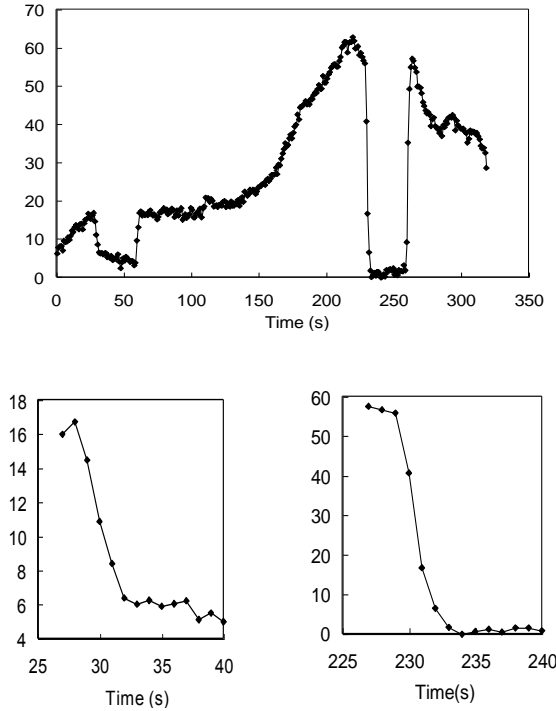
Fig. 3 Analysis of the relaxation process following a stop of the barrier during compression in two monolayer states: left – constituent molecules are loosely packed in a 2D gaseous phase, right – molecules are fairly ordered in a 2D solid phase. Displacement current is indicated in fA.

The dielectric relaxation time, i.e. the period needed for the monolayer to acquire a new equilibrium state, depends on the molecular area A and hence on the molecular orientational order. At the beginning of the compression, in a 2D gaseous phase with a low orientational order the transient process is relatively slow ($\tau \sim 3$ s). On the other hand, in the state when the molecules stand upright at the air/water interface, the monolayer responds to the external compression stimulation much faster ($\tau \sim 1$ s). This observation can be supported by the theoretical consideration based on the Debye theory for

studying the rotational Brownian motion of molecules with permanent electric dipoles expressed by the rotational Debye-Brownian equation (2)

$$\frac{\delta \omega(\theta,t)}{\delta t} = \frac{1}{\xi \sin \theta} \frac{\delta}{\delta t} \left[\sin \theta \left(kT \frac{\delta \omega}{\delta \theta} + V \sin \theta \omega(\theta,t) \right) \right]$$

where $\omega(\theta,t)$ is the probability function representing the probability of the molecules standing on a water surface at a tilt angle θ at time t. ξ is the friction constant of monolayer and V the interaction form function excluding the angular portion. Only dipole-dipole interaction and equivalent additional piezoelectric interaction energy are taken into consideration. With the orientational order parameter of monolayers on a water surface, which is defined as

$$S = \int_0^{\theta_A} \cos \theta \omega(\theta,t) \sin \theta dt, \tag{3}$$

eq. (2) can be used to find the order parameter S during monolayer compression. In order to examine the dielectric relaxation phenomena by monolayer compression, we assume here that a step additional interaction $RU(A_i - A)$ is produced in monolayers as a result of piezoelectric effect, starting from an arbitrary equilibrium state at the molecular area $A = A_i$ by monolayer compression. R is the interaction parameter, and $U(A_i$--$A)$ is a unit step function. As shown in [3] the calculation of the relaxation time τ becomes

$$\tau = \frac{\xi}{4kT} \frac{1 - \cos \theta_A}{2 + \cos \theta_A} \tag{4}$$

In this model we assume that the motion of rodlike polar molecules is restricted within a cone $0 \le \theta \le \theta_A$, where $\theta_A = \arcsin \sqrt{A/A_C}$, principally due to effects of hard core intermolecular forces. A_C is the critical molecular area (πd^2) at which molecules lying on a water surface due to the dipole-water surface interaction stand up by monolayer compression.

The length of the molecular long axis l is estimated as 25 Å by MM2 molecular dynamics simulations. In eq. 4, the value of ξ was found 6×10^{-18} Js. The results quantitatively support the above-formulated expectation that the dielectric relaxation time τ is inversely proportional to the polar orientational order and the molecular packing, which favors the intermolecular energy exchange during relaxation.
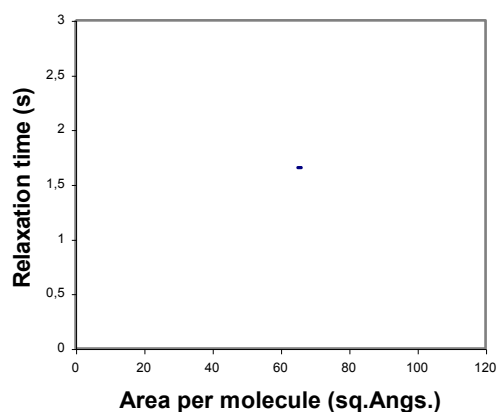
Fig. 4 Relaxation time isotherm as evaluated from Eq. 4.

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BIOGRAPHY

Július Cirák (Assoc. Prof., Dipl. Eng., PhD.), born in Likier, in 1953, graduated from the Faculty of Electrical Engineering, Slovak University of Technology, Bratislava, in 1976, and received the PhD. Degree in experimental physics, in 1981. Since 1988 he has been working as Associate Professor at the Department of Physics of the Faculty of Electrical Engineering and Information Technology STU Bratislava. His research activity is oriented to organic molecular materials: formation of ultrah-thin films and investigation of their properties.

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