

DYNAMIC BEHAVIOUR OF THE LANGMUIR MONOLAYER AT THE AIR/WATER INTERFACE

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The experimental results of the measurements of displacement current generated during stearic acid monolayer compression are analyzed by means of the model based on analogy with non-ideal gas of polar rod-like molecules, assuming Boltzmann statistics of orientational distribution. The experimental data are compared with our theory and the following experimental steps as well as further theoretical analysis are suggested.

Keywords: Langmuir film, non-ideal gas approximation, order parameter

1 INTRODUCTION

Over the past ten years the displacement current measuring technique for the dynamical study of monolayers was developed [1]. With this technique, displacement current generated from changes in vertical component of the dipole moment of monolayer by the increasing of surface pressure was found to be detected with high sensitivity.

The change of orientational polarization vector can be expressed as Maxwell's displacement current through a short-circuited capacitor being formed by two parallel plates, one in above the monolayer detached at a certain spacing, another immersed in water below the monolayer [2]. During the compression of the monolayer, the external mechanical force, which drives a movable barrier, results in the change of surface concentration of the molecules as well as in the orientational change of the direction of the molecular electric dipoles.

The theoretical explanation of the behaviour of a similar system can be found in [3]. This is based on the well-known theory of the Debye-Brown rotational motion [4]. In this communication our previous experimental results are analyzed using an elaborated theoretical model.

2 EXPERIMENTAL

The experimental method consists in detection of a transient electrical effect arising on two parallel electrodes, between which an organic monomolecular layer formed of straight-chain hydrocarbons is placed. Stearic acid (SA) was purchased from Lachema (Brno, Czech Rep.).

Each substance was dissolved in chloroform (as a 1 mmol/l solution) and added to a surface of bidistilled water (12 MΩcm) to form a single monolayer. The Langmuir trough was supplied from NIMA Tech-

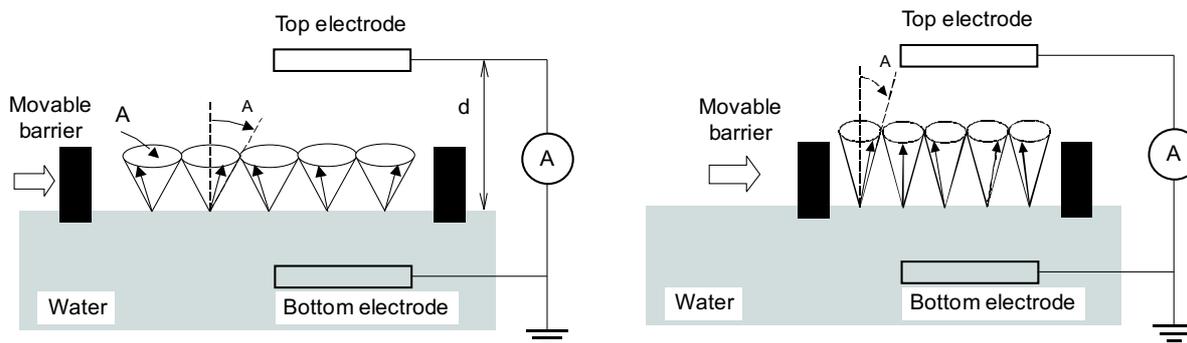


Fig. 1. Schematic view of the experimental setup for displacement current measurement. Rod-like polar molecules execute precessional motion at the water surface with maximal tilt angle Θ_A (A and μ stands as area per molecule and dipole moment of molecule, respectively).

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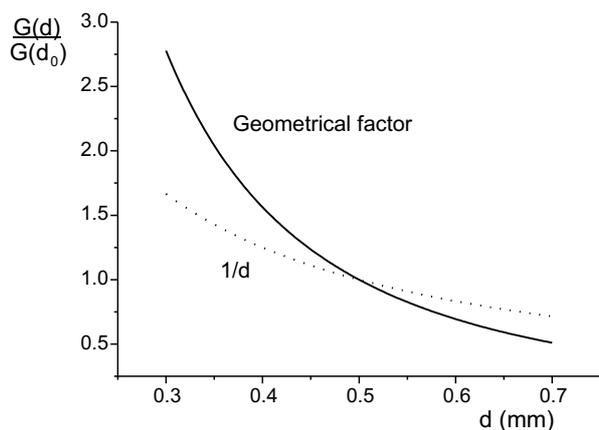


Fig. 2. Comparison of geometrical factor (5) and reciprocal distance.

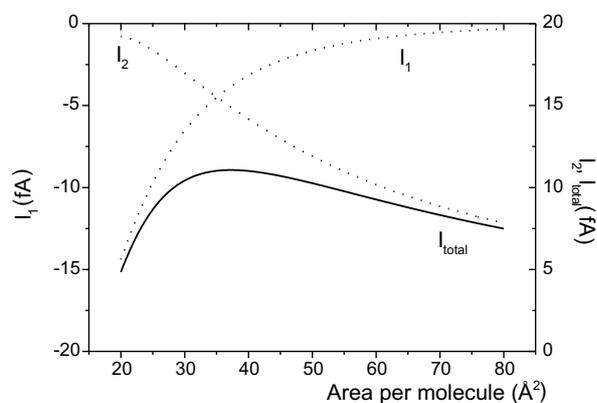


Fig. 3. Two contributions I_1 and I_2 to the overall current.

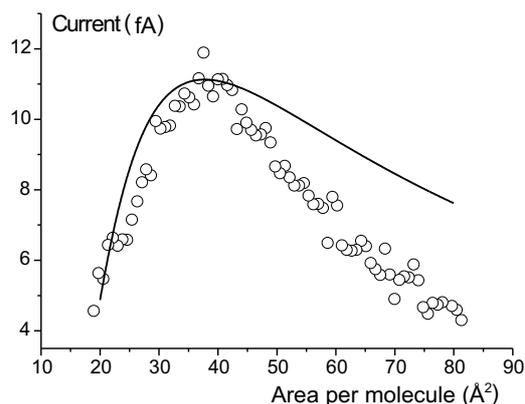


Fig. 4. Comparison of typical experimental results obtained on the stearic acid monolayer with our calculations.

nology, UK. The total working area of the trough was 600 cm^2 and the compression rates were varied between 20 and 120 cm^2 and which corresponding to about 0.05 to $0.30 \text{ Å}^2/\text{s}$ per molecule.

A schematic diagram of the displacement current apparatus is depicted in Fig. 1. It is a special configuration

designed for the detection of electrical transient processes in the floating monomolecular layer at the air/water interface. Two plate electrodes form the basis of the setup. Upper electrode is electrically shielded, suspended in air at a spacing about $d = 0.5 \text{ mm}$. Bottom electrode is immersed in water (sub-phase in the Lagmuir trough) and grounded. Due to dynamic processes in the monolayer associated with the change of charge distribution, the charge Q_j induced in the upper electrode varies with time and this generates a current flowing through a sensitive electrometer (Keithley 617). The detection system is attached to the computer-controlled Lagmuir trough being electrically shielded and placed in a dust-free compartment on an anti-vibrating stand.

Measurements were carried out at various speeds of compression. A position of the measured maximal current flowing between the electrodes for different rates of compression is situated at same values of the area per molecule (Fig. 5a).

3 CALCULATIONS

The model is based on the assumption that each molecule behaves like a weak dipole moment with a negative pole bound to the water surface. In [5] it is shown that for a linear hydrocarbon chain the description of electric properties using the dipole approximation is sufficient. The influence of the polar water molecules on a final measured signal was neglected. A basic assumption of the model is that the individual dipole moments have random directions within a certain solid angle. The molecules execute a random precessional motion with a maximal possible dipole moment tilt Θ_A from the vertical axis. The angle Θ_A is defined by the relation $\cos \Theta_A = \sqrt{1 - A/A_c}$, where A is the area per molecule and A_c is the critical area per a molecule lying on the water surface [3]. Generally, we consider the molecule as a rod-like rigid body without a possibility of bending.

The statistical mean value of $\cos \Theta$, where Θ is the angle between the vector dipole moment and the vertical axis, is defined by relation

$$\langle \cos \Theta \rangle = \frac{1}{2} \int \cos \Theta \exp\left(-\frac{\bar{U}}{kT}\right) d\Omega \quad (1)$$

where $d\Omega$ is a solid angle in which the molecule is laying and the \bar{U} is the mean value of interaction energy. The angle Θ varies as $\Theta \in \langle 0, \Theta_A \rangle$.

The mutual interactions between molecules consists of two-body dipole-dipole interaction similar to one in the non-ideal gas theory, *eg* on the deduction of van der Waals equation of state. Other potential energy components of the system (repulsive and dispersive) are expressed by well-known Buckingham modified potential.

$$U = C \exp\left(-\frac{r}{r_0}\right) - \frac{B}{r^6} + \frac{\mu' \mu''}{4\pi\epsilon_0 r^3} [\boldsymbol{\nu}' \cdot \boldsymbol{\nu}'' - 3(\boldsymbol{\nu}' \cdot \mathbf{n})(\mathbf{n} \cdot \boldsymbol{\nu}'')] \quad (2)$$

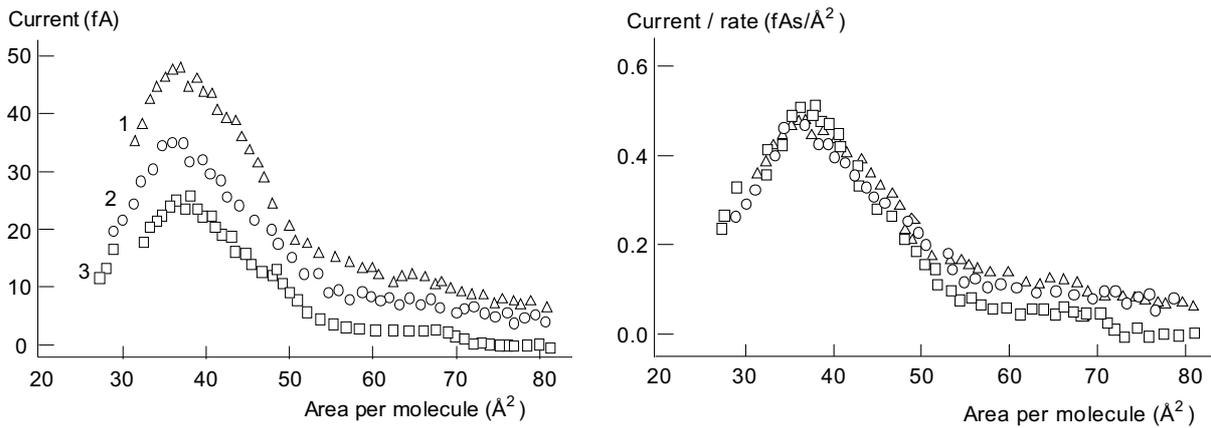


Fig. 5. a) Recordings signals obtained at three different rates of compression: (1) 100 cm²/min, (2) 75 cm²/min, (3) 50 cm²/min. b) The family of signals from Fig. 5a re-plotted as the dependence I/β versus area per molecule.

where μ' , μ'' are dipole moments with the base direction vectors ν' , ν'' and vector \mathbf{n} connects the polar heads of a chosen pair of molecules. The intermolecular distance r is defined as a center-to-center separation of the particles ($|\mathbf{n}| = r$) and C , B , r_0 are constants. For empirical and semi-empirical two-body potentials the many-body effect will implicitly be included by justification of parameters with experimental obtained data [6]. For the mean value of interaction energy we can obtain

$$\bar{U} = C \exp\left(-\frac{r}{r_0}\right) - \frac{B}{r^6} - \frac{\mu'\mu''}{4\pi\epsilon_0 r^3} (1 - \cos \Theta_A) \quad (3)$$

If we assume $|\bar{U}| \ll kT$, the integral has an analytic solution and we can expand the exponential function in a series where we take only first two terms into consideration.

If we consider the organic film as a system of electric dipole moments then it is possible to calculate the induced charge on the upper electrode with the method of images

$$Q_i = \langle \mu_z \rangle N G = \mu \langle \cos \Theta \rangle N G \quad (4)$$

where G is the geometrical factor for the experimental setup and N is the number of molecules under the electrode. For a circular electrode was found geometrical factor

$$G = \frac{8d}{3L^2} - \frac{4\sqrt{d^2 + L^2}(2d^2 - L^2)}{3d^2L^2} \quad (5)$$

where L is the radius of the electrode. The dependence G on a distance is shown together with a factor $1/d$ introduced in [3] on Fig. 2.

The current flowing between the electrodes can be obtained as a time change of the induced charge

$$I = \frac{\partial Q_i}{\partial t} = G\mu N \frac{\partial \langle \cos \Theta \rangle}{\partial t} + G\mu \langle \cos \Theta \rangle \frac{\partial N}{\partial t} = I_1 + I_2. \quad (6)$$

The two contributions to the overall current can be consequently represented in Fig. 3.

4 DISCUSSION

Let us turn our attention on basic equation which was introduced in [2]

$$I = \frac{\mu_z}{d} \frac{\partial N}{\partial t} + \frac{N}{d} \frac{\partial \mu_z}{\partial t} + C \frac{\partial \Phi_s}{\partial t} \quad (7)$$

where C is the capacitance between upper electrode and water surface and Φ_s is the surface potential of water. The third component was taken as zero because the surface potential of water may be consider constant during the experiment. Our expression (6) closely corresponds to (7), the individual terms being expressed in more details.

A comparison of typical measured data obtained on mono-layers formed with stearic acid molecules with our theoretical model is shown in Fig. 4.

Measurements recorded at various rates of compression are presented in Fig. 5a. The calculation predicts a position stability of the measured maximum in the dependence of I on the area per molecule A for various rates of compression β and a ratio

$$\frac{I_1}{\beta_1} = \frac{I_2}{\beta_2} = \dots$$

is conserved. This theoretical prediction was fully confirmed by the experiment (Fig. 5b).

4 CONCLUSIONS

We rather successfully explained the experimental data by analyzing the model, based on the analogy with a non-ideal gas. This approximation can be justified for the assembly with weak intermolecular forces even though the concentration of particles is higher then in a real gas.

The concentration gradient generated during compression is not included in this model. Therefore, it was not possible to calculate relaxation effects in the ordering after stopping the compression.

The difference between the calculations and the experiment for larger intermolecular distances is probably caused by an omission of the interaction between the monolayer and the sub-phase (water in our case) and the contribution of the sub-phase to the total dipole moment. The formula used for Buckingham potential is also not absolutely correct when the tilt angle of any dipole deviates significantly from zero.

In future, we intend to utilize a method based on the cluster interaction potential and the equation of state.

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The young scientist competition will be organized at MIKON Conference. The papers approved for presentation during Conference, and entering the competition, are to be evaluated for content, presentation manner and visual aspects. Three best works are to be awarded by the Polish IEEE Chapters. Eligible candidates *ie*, students, PhD students or young engineers, under 35 years of age, must be the main authors and they must present their original works, at oral or poster Conference sessions. In the case of a paper co-authored by an advisor, the latter should sign the declaration - to be attached to the submission - that the work is primarily the one of the candidate.

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