

Influence of alcohol on mechanical and electrical properties of thin organic films*

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Abstract: Stability of organic materials properties is essential for further applications and was intensely investigated in last few decades. The aim of this study is to detect the structural changes of dipalmitoyl-phosphatidylcholine (DPPC) monolayer as a model system of organic material under influence of alcohols solutions. As subphases of monolayers (Langmuir films), pure water, ethanol and methanol solutions were used. For detection of changes in charge states of the molecules as well as relation with structural and conformational changes, a contactless method employing Maxwell's displacement currents (MDC) was used. In DPPC monolayer on the subphase of methanol-water, a gradual absorption of methanol molecules into the layer can appear. In DPPC monolayer on the subphase of ethanol-water adsorption of ethanol molecules on the layer can be observed. Influence of alcohols results in a significant change of mechanical and electrical properties as well as in the stability of thin films.

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1 Introduction

The great challenge of material sciences in last the decade is application of new organic and nanostructured materials. The insoluble monolayers of surfactants at the air/liquid interface (Langmuir films) exhibit very interesting physical properties attributed to low-dimensional systems. In the Langmuir–Blodgett (LB) technique a well-ordered monomolecular layer of amphiphilic organic material is prepared at the air/water interface by the movable barrier to a specified surface pressure-area state and then transferred to a solid substrate. Investigation of such monolayers is interesting also from the point of view of semiconductor technique, optoelectronic equipments and polymers. For all these applications it is usually necessary to have a uniform film with well-defined parameters prepared by a reproducible technique. Therefore, the essential requirement is the stability of mechanical and chemical properties in thermal, mechanical or chemical stress.

To study structural properties and the organization of organic monolayers at the air-water interface, several techniques have been developed [1, 2]. To examine changes in the charge of molecules related to their structural properties, a contactless method has been developed (MDC). Application of MDC technique and its utilization in the study of the structural, electrical and mechanical changes in biological samples was used for the first time in our work [3].

2 Materials and methods

2.1 Materials

The material used in this study as model phospholipid was 1,2-dipalmitoyl-sn-glycero-3-phosphocholine monohydrate (DPPC) purchased from Sigma-Aldrich. Lipid was dissolved in chloroform at the stock concentration 0.5 mg/mL and spread on the subphase using microsyringer (Hamilton, USA). Pure water (bidistilled deionized water, 15 M Ω ·cm) was used as a subphase. The subphase was maintained by thermostat at the temperature of 17°C; monolayer was allowed to equilibrate and the solvent allowed to evaporate for 15 minutes.

2.2 Methods

The basic method for evaluation of properties of the organic monolayer situated on the air/water interface is surface pressure measurement.

The surface pressure-area ($\Pi - A$) isotherms were measured by the Willhelmy plate method using surface pressure sensor PS4 (Nima Technology, UK) with accuracy ± 0.05 mN/m. Consequently various mechanical and thermodynamic properties such as elastic modulus of Langmuir films or thermodynamic properties (Gibbs free energy, entropy and enthalpy) can be evaluated.

The elastic modulus E (also called reciprocal compressibility C^{-1}) represents the

consistency of the monolayer and, in analogy with bulk materials is defined as

$$E = -A \left(\frac{\partial \Pi}{\partial A} \right)_T, \quad (1)$$

where Π is the surface pressure, A the area per molecule and T the temperature. The elastic modulus expresses the elasticity of the Langmuir film under influence of the compression force. The stability of the mixed monolayer can be determined by evaluation of the Gibbs free energy G by integration of surface pressure - area isotherm up to the selected surface pressure

$$G = \int_0^\Pi A d\Pi, \quad (2)$$

where A is the molecular area and Π surface pressure.

For detection of changes in charge states of the molecules as well as the relation with structural and conformational changes, a contactless method was developed based on an analysis of Maxwell's displacement currents (MDC). This method was originally introduced by Iwamoto et al. [1, 2] and improved by other authors [4–7]. Proposal of MDC experiment application for biological membrane phantom measurement was presented for the first time in our previous work [16].

The basic components of the Maxwell's displacement current - experimental setup attached to the computer-controlled model Langmuir trough (model 611, Nima Technology, UK) are schematically shown in Fig. 1. The top electrode was situated in air, parallel to the interface, without a direct mechanical or electrical contact with a floating monolayer on the water surface. The air gap between the top electrode and the water surface was regulated to a certain spacing (approx. 1 mm) by measuring the capacitance of the electrode system. The displacement current was detected with a Keithley 617 electrometer (Keithley Instruments, Cleveland, Ohio, USA). The sensitivity of measuring the current was 0.1 fA, the background noise was suppressed by a multiple electrical shielding of electrode as well as whole measuring system to 2 fA. Langmuir trough was situated in a laminar-flow box on an antivibrating stand to avoid any mechanical stress. The total working area of the trough was 600 cm² and the compression rate was 50 cm²/min, which correspond to 1.7 × 10⁻³ nm²/s per one molecule. The area of the top electrode was $A_e = 20$ cm².

Due to dynamic processes in the monolayer associated with the change in charge distribution caused by its compression, the induced charge in the top electrode varies with time and this generates a current flowing through the outer circuit via the electrometer.

As we showed in our previous studies [8] the current I flowing in the outer circuit can be expressed as a time derivative of the induced charge

$$I = \frac{\partial Q}{\partial t} = \mu N g \frac{\partial \langle \cos \Theta \rangle}{\partial t} + \mu \langle \cos \Theta \rangle g \frac{\partial N}{\partial t}, \quad (3)$$

where μ is the dipole moment of one molecule, N is the number of molecules under the top electrode and g is the geometrical factor depending only on the distance between the top electrode and the top plane of the monolayer and on the shape and area of the upper

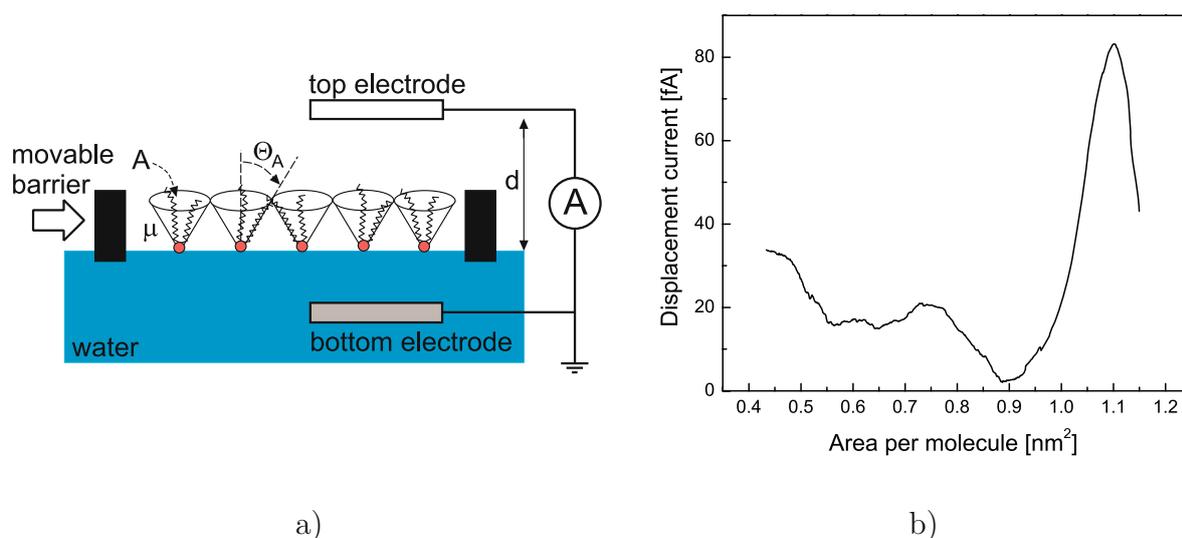


Fig. 1 Schematic view of the experimental setup for displacement current measurement (a). Rod-like polar molecules execute precessional motion at the water surface with maximal tilt angle Θ_A (A and μ stand for the area per molecule and the dipole moment of molecule, respectively). Displacement current measurement - area per molecule isotherm of DPPC monolayer at the water surface (b). The current peak at value around 1.1nm^2 represents structural phase transition of the monolayer.

electrode. The $\langle \cos \Theta \rangle$ stands for the statistical mean value $\cos \Theta$ where Θ is the angle between the direction of the dipole moment and the normal.

By integrating the displacement current with respect to time, the induced charge Q can be obtained and in this way we also evaluated the vertical component of the molecular dipole moment. Thus, the dipole moment projection to the normal $\mu_z = \mu \langle \cos \Theta \rangle$ should be calculated as

$$\mu_z = \frac{1}{gN} \int_0^t I dt. \quad (4)$$

In contrast with surface pressure - area isotherm analysis in MDC measurement is extremely sensitive also in the low surface pressure area, where surface pressure methods are useless. Comparison of surface pressure - area and dipole moment projection - area isotherms is shown in Fig. 2.

3 Experimental results

3.1 Electrical properties

By analysis of records of the Maxwell displacement current projection, we can calculate the dependence of the dipole moment on the area per molecule of the monolayer. DPPC monolayer at the water surface shows a rapid change of the dipole moment projection at value around 1.1 nm^2 (Fig. 2b).

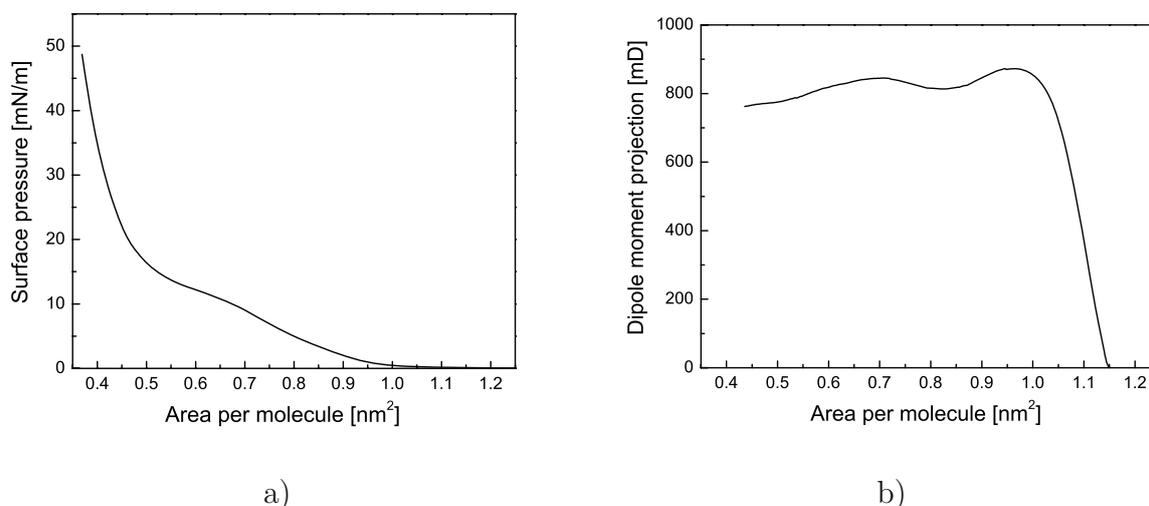


Fig. 2 Surface pressure - area per molecule isotherm of DPPC monolayer at the water surface (a). Dipole moment projection - area per molecule isotherm of DPPC monolayer at the water surface (b). Increase of surface pressure as well as dipole moment projection at value around 1.1 nm^2 represents structural phase transition of the monolayer.

This change represents a phase transition of the Langmuir film from gaseous phase to liquid phase [9]. From results of the measurement of the surface potential by Kelvin probe [10] the value of the dipole moment of DPPC molecule was determined to be 820 mD. Our recordings show the value around 815–825 mD, which is in accordance with values obtained by independent measurements.

At subphase ethanol - water, a significant change in the dipole moment projection of DPPC molecules forming the monolayer appeared (Fig. 3b). Monolayer exhibits a very sharp phase transition from gaseous to liquid phase at area about 0.8 nm^2 (observable only for first compression) and from liquid phase to solid phase at 0.5 nm^2 .

Similarly, as at DPPC monolayer on the subphase methanol - water we can observe a time shift of $\pi - A$ isotherm to higher values. However, this shift is not as obvious as it was at DPPC monolayer on the subphase methanol - water (Fig. 3a).

3.2 Mechanical and thermodynamical properties

Mechanical properties were evaluated in accordance with the above-mentioned analysis. Fig. 4 depicts the time dependence relationship between Gibbs free energy (a) and elastic modulus - area isotherms (b) situated on methanol (up) and ethanol (down) subphase.

Time dependence of the Gibbs free energy is shown in Fig. 4a. In accordance with Eq. 2, its change is directly proportional to the adsorbed alcohol (via change of molar ratio of alcohol in the monolayer). Therefore continuous adsorption of alcohol molecules for both cases is observable in DPPC monolayer. The Gibbs free energy characterizes the stability of the phospholipid/alcohol mixture. Alcohol molecules change the monolayer,

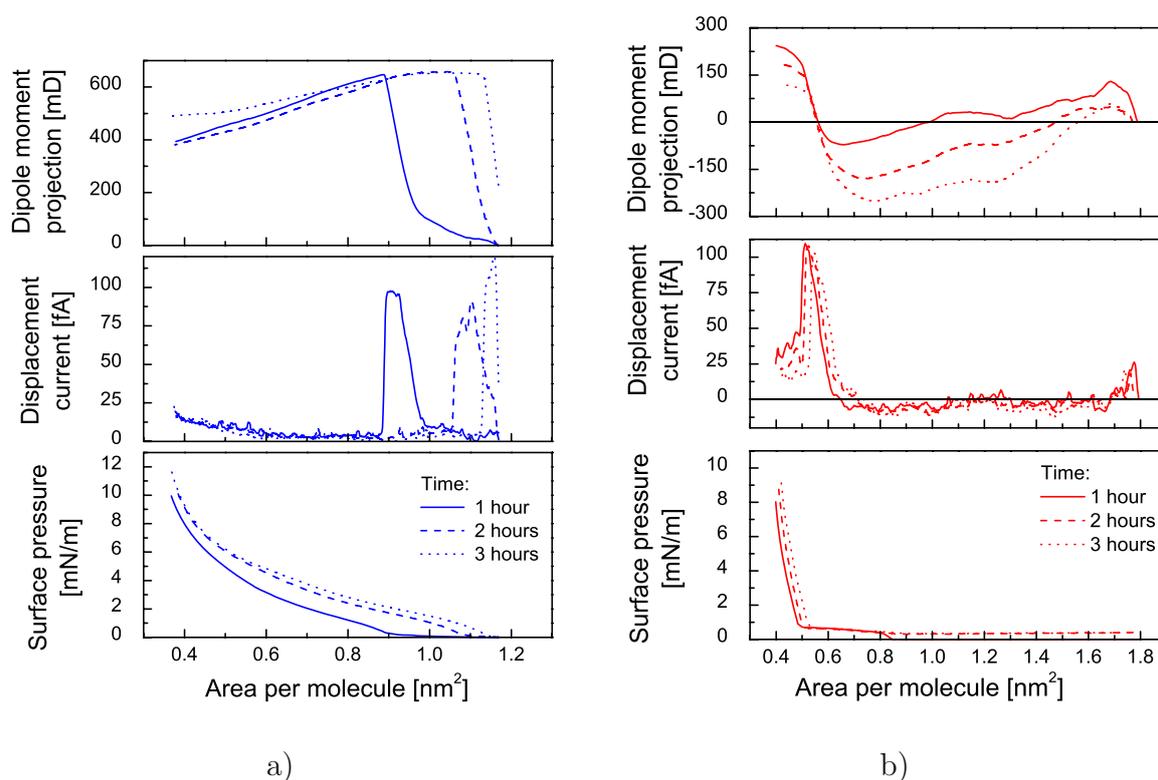


Fig. 3 Surface pressure - area (bottom), displacement current - area and dipole moment projection - area (top) isotherms of DPPC monolayer. Monolayers were situated on methanol (a) and ethanol (b) subphase.

because incorporation into the monolayer carry to lower free energy. For the sake of comparison, for DPPC monolayer situated on pure water it was found to have the value of 4.92 kJ/mol. The decrease of energy indicates the preference of alcohol adsorption.

Time dependence of the adsorption process can be described by the Ward and Tordai equation estimate for diffusion-controlled adsorption kinetics

$$\Gamma(t) = \sqrt{\frac{D}{\pi}} \left(2c_0\sqrt{t} - \int_0^t \frac{c_s(\tau)}{\sqrt{t-\tau}} dt \right), \quad (5)$$

where $\Gamma = 1/A$ is the surface concentration in time t , D the diffusion constant, c the alcohol concentration in bulk subphase and τ is a dummy variable.

Because of difficulties in solving Eq. (5), an asymptotic model for the short time limit (or a slow adsorption) has been proposed by Fainermann et al. [12] in the form

$$\Gamma(t) = 2c_0\sqrt{\frac{Dt}{\pi}}. \quad (6)$$

Since the Gibbs energy in our case expresses the degree of adsorption, we can rewrite this relation as

$$G(t) \propto \sqrt{\frac{Dt}{\pi}}. \quad (7)$$

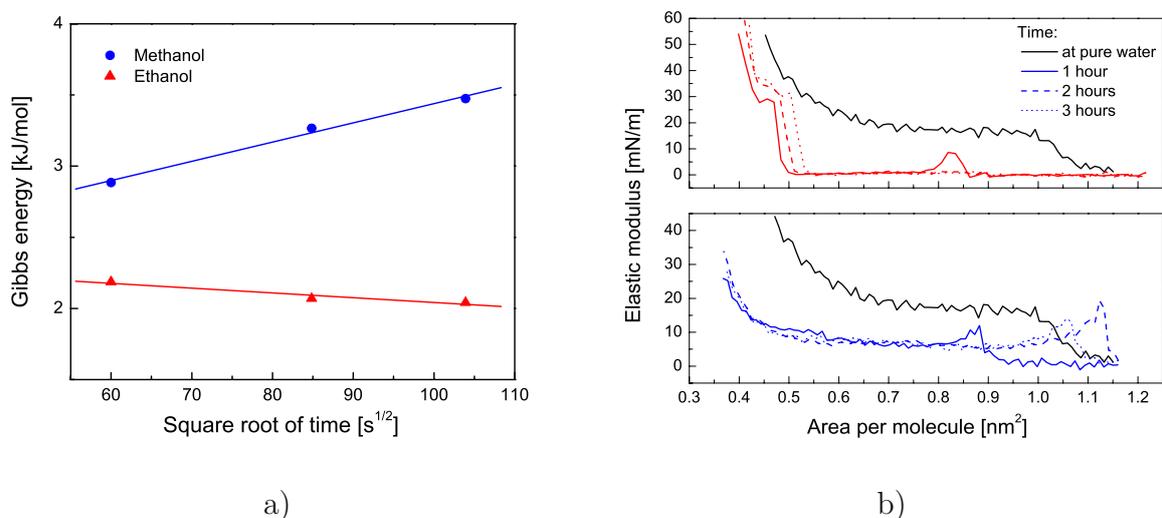


Fig. 4 Gibbs free energy - time dependence (a) and elastic modulus - area isotherms (b) situated on methanol (up) and ethanol (down) subphase. Gibbs free energy as a function of time is analyzed for surface pressure of 8 mN/m. Solid lines represent calculated values for the adsorption process (see Eq. (7)). Elastic modulus is calculated for various times. For a comparison, the elastic modulus of DPPC monolayer on the pure water (black solid line) is also shown.

The diffusion process can be studied in this manner, and it is possible to obtain diffusion constants: for methanol $D = 5.73 \times 10^{-4} \pm 4.83 \times 10^{-6} \text{ m}^2/\text{s}$ and ethanol $D = 3.59 \times 10^{-5} \pm 2.53 \times 10^{-6} \text{ m}^2/\text{s}$.

From the graph representing the relation between elasticity modules and area per molecule, Fig. 4b, we found that at DPPC monolayer on the surface of both subphases (ethanol-water and methanol-water) the elasticity modulus of the monolayer decreases. Our results suggest a gradual increase of membrane fluidity. Molecular interaction can be studied by elastic modulus - surface pressure isotherm shown in Fig. 5. Elastic modulus has a strong dependence on surface pressure and the local minimum in this dependence is usually taken to be related to the phase transitions and/or coexistence region (intermediate phase) [13]. Therefore until two phases coexist, monolayer compression result only in phase transition and no elastic modulus increase is observed.

Nevertheless the elastic modulus characterizes the intermolecular forces. For comparison, a hard sphere model is shown in Fig. 5. The ideal for the model is based on the assumption of hard sphere compression. Accordingly it is possible to write the elastic modulus in the form

$$E_{model} = \frac{E}{1 - A_{excl}/A}, \quad (8)$$

where A_{excl} is the excluded area of incompressible spheres. In this way the excess over this contribution represents molecular interaction. For our case the excluded area of 0.35 for the model was used.

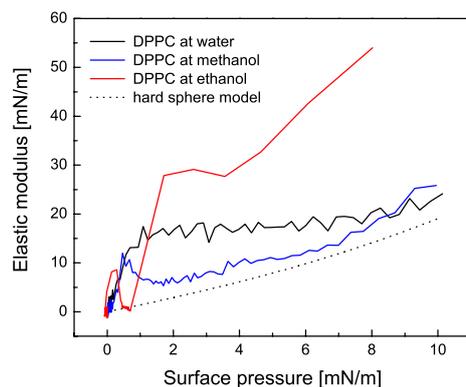


Fig. 5 Elastic modulus versus surface pressure (for measurement after 1 hour). Solid line represents various subphases (see insets for details), the dotted one represents a hard sphere model with excluded area of 0.35 nm^2).

4 Discussion

At subphase ethanol - water the DPPC monolayer exhibits a very sharp phase transition from gaseous to liquid phase. The phase transition is usually caused by the presence and/or the amount of surfactant in air-liquid interface. Cruz et al. [14] investigated the influence of pulmonary surfactant protein (*SP-B*) and the distribution of liquid-expanded (*LE*) and liquid-condensed (*LC*) regions of DPPC and DPPC/DPPG (dipalmitoylphosphatidylglycerol). They found that increasing amounts of *SP-B* caused increasing amounts of *LC* microdomains and their size decreased in both DPPC and DPPC/DPPG films. As we observed no time shift of the dipole moment projection, we assume that the distance between molecules does not increase. Unlike DPPC monolayer on the subphase methanol - water, adsorption of ethanol to this layer might occur. Yamamoto et al. [15] investigated the interaction with DPPC and dihexadecyl phosphate with ethanol. They found a different behaviour of ethanol/water solution depending on its concentration.

At DPPC monolayer on the surface of subphase methanol - water no significant changes of the dipole moment projection of the DPPC molecule appear when compared to the dipole moment projection of the DPPC molecule on water, even though the effect of subphase methanol - water is obvious. From the results of time shift of the area per DPPC molecule to higher values it can be inferred that DPPC molecules move away from each other leading to incorporation (penetration) of methanol molecules into the air - liquid interface [16–20].

The time evolution of the Gibbs energy gives information about monolayer stability as well as diffusion process. For both alcohols a continual adsorption process was observed and diffusion constants were estimated. Comparison with the Gibbs energy of monolayer situated on pure water indicate energetically preferable process.

From the graph representing the relation between elasticity modulus and area per

molecule of DPPC monolayer on the surface of both subphases (ethanol - water and methanol - water) we found that the elastic modulus of the monolayer decreases. Elastic modulus - surface pressure isotherms reflect intermolecular interaction as well as phase transition. For a water-methanol subphase the phase transition is shifted to lower surface pressures and molecular interaction decreases to the necessary limit represented by the hard spheres model. In contrast to these results, a similar shift of phase transition is observed for DPPC situated on water-ethanol subphase, and a stronger molecular interaction is noticeable.

Based on our results we assume a gradual “solidification” of the membrane and loss of its elasticity [21, 22]. Increase of rigidity is proportional to alcohol length, which is in agreement with other studies [16].

5 Summary

Behaviour of a thin organic film under influence of alcohol stress is investigated. Monomolecular film properties representing by DPPC molecules on two different subphases is substantially different. In DPPC monolayer on the subphase of methanol - water, a gradual absorption (incorporation) of methanol molecules into the layer can appear leading to “dilution” of the layer and thus to the change of monolayer permeability. In DPPC monolayer on the subphase of ethanol - water, adsorption of ethanol molecules to the layer can be observed leading to the change of electric properties of the layer surface. Consequently, the membrane permeability might change. At both subphases (ethanol - water and methanol - water) the elasticity modulus of the monolayer decreases leading to the increase of membrane fluidity in low surface pressure region.

This study is substantial for organic thin film applications, because requirement on chemical stability of electrical and mechanical properties are essential.

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