Phase transitions in phospholipid monolayers and rheological properties of the corresponding membrane model

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Abstract: Insoluble spread monolayers of Dipalmitoyllecithin and Dipalmitoylcephalin are investigated by \( \pi /A \) isotherms and periodic compression and dilatation to determine their elasticity and the phase angles between strain and stress.

Depending upon the temperature, the phase angle becomes noticeable in the film pressure region in which the phase transition takes place.

From the rheological point of view, we conclude that the relaxation processes in the two-phase film state make the main contribution to the phase angle.

Key words: Phospholipid monolayers, phase transition, pressure-area isotherms, surface rheology, marangoni effect

1. Introduction

This paper deals with measurements of surface rheological properties in connection with the behavior of phospholipid bilayers that consist of different states. Phospholipid bilayers are well-known examples of biological membranes. One of the main questions is the relevance of monolayer studies to the properties of bilayers. Bilayers hold forces in the normal direction of the separated monolayers. These interaction forces cannot be simulated by monolayer experiments. For membrane deformations produced at slow strain rates with no permanent material alteration due to the membrane forces, elastic effects are reasonable representations of the material character of the membrane. However, if the rate of deformations increases, thermodynamically irreversible processes which result from internal friction and heat dissipation within the membrane become evident. The time dependence of the force relaxation is determined by the rate of viscous dissipation and the lateral transport processes of matter. The latter is forced by a compression or dilatation of each monolayer. A simple experiment will show this situation. A thin bilayer film is fixed in a frame and one of the wires is forced to oscillate. The film will be stretched and compressed periodically. During this process the concentration of the film-forming molecules may increase and decrease more near the movable barrier than far from it. Therefore a surface-pressure gradient results. The compensation of such a gradient, named the Marangoni Effect, takes place by lateral transport of the film components.

This process is characterized by the relaxation time of the pressure gradient.

If the relaxation time becomes greater than the time for a period of compression and dilatation of the monolayer, a phase angle between strain and stress occurs. This relationship can be described by a complex modulus of the monolayer elasticity.

\[
e = \frac{-d\pi}{d \ln A} = e' + i e'' = |e| \cos \alpha + i |e| \sin \alpha ,
\]

where \( A \) is the area of the film.

Experiments and mathematical analysis of the Marangoni Effect for phospholipid films were published by Dimitrov et al. [1]. The static, or better the quasistatic, \( \pi /A \) isotherms of spread and compressed phospholipid films at different temperatures offer some fundamental problems. Some of these are related to the phase transition regions and to the hysteresis effects.

Surveys of this problem are given by Nagle [2] and Dörfler [3].

According to Erbrich, Septinus, and Zimmermann, the phase transition is characterized by a two-phase region in which liquid expanded and condensed domains exist [4]. The equilibrium between these two film states depends on the pressure which acts on the film. This process induces a characteristic time. If this
time becomes greater than the time for a period of compression and dilatation of the film, a relaxation appears which can be observed by the phase angle \( \alpha \) between strain and stress.

The imaginary part of Eq. (1) leads to

\[
\eta_d = \frac{|\varepsilon| \sin \alpha}{\omega}, \quad \text{where} \quad \varepsilon = \frac{-d\pi}{dA} \cdot A.
\] (2)

From the works of Van den Tempel [5], Lucassen [6], Lucassen-Reynders [7], Kretzschmar, Lunkenheimer, and Miller [8], it is well known that the contribution of mass transfer between interface and bulk is made by altering the area of interface continuously or periodically. This is due to the propagation of transverse and longitudinal waves or radial oscillating bubbles. Here the phase angle \( \alpha \) between strain and stress is the consequence of the vertical diffusion exchange. Less work has been published about the lateral transport processes triggered by a compression or dilation of a monolayer. Vollhardt and Wüstneck investigated long-chain fatty acids [9] and the special case of phospholipids is shown in ref. [1]. The initial state for our problem is the observed hysteresis in \( \pi /A \) isotherms of spread phospholipids. Phospholipids show phase transitions between so-called liquid expanded and liquid condensed films that depend upon the chain lengths and the chemistry of their head groups. In the phase transition region the \( \pi /A \) curves show plateau sections and concave slopes. Erbrich et al. [4] show that the phase transition region is distinguished by an equilibrium between the two adjacent phases. In other words, a two-phase region which contains liquid expanded and liquid condensed domains exists. The conversion is a rate-determining step in the registration of \( \pi /A \) isotherms and leads to a noticeable phase angle between strain and stress. It means a difference between the \( \pi /A \) curves in the region of phase transition exists that is obtained by compression and dilatation. The aim of this paper is to show the possibility of detecting the phase-transition region by the method of surface rheology. The principle complications in detecting the phase transition by static \( \pi /A \) isotherms have been shown by Nagle [2]. In [4] plot \( A \) vs. \( T \) for different values of \( \pi \) as a constant parameter is used. Generally the phase transition shifts to a higher film pressure if the temperature increases.

2. Experimental

For measuring the retardation of the equilibrium in film pressure along the x-axis we used a device which was described by Kretzschmar and König [10] and is similar to the equipment of Van Voorst Vader [11], Van den Tempel [12], and Wasan [13]. The principle of the apparatus is shown in Fig. 1.

In the first step of the experiments the chromatographically purified DL-\( \beta,\gamma \)-Dipalmitoyl-\( \alpha \)-Lecithin