



Thin liquid films in biomedical studies

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ABSTRACT

Some main findings in the area of thin liquid films (TLF) in biological and medical science are reviewed and discussed. In a brief explanation of symmetrical and asymmetrical TLF, their formation and stability are presented. The main achievements in studies of films from phospholipid, protein and lipid–protein natural mixtures are summarized. Special attention is devoted to foam films composed of pulmonary surfactant and its constituents at the air–liquid interface since black foam film model offers new opportunities for studying the structure and stability of surfactant layer on the alveolar surface.

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1. Introduction

Surface and colloid science continues to play an important role in the investigation of interfaces in biological systems and provides effectively transferring well-established knowledge in the area. It allows to clarify the basic processes such as formation, stability and permeability of biointerfaces and membranes, biomembrane adhesion and fusion, intermolecular recognitions, etc. The achievements of surface and colloid science open new directions for medical application in diagnostics, biomacromolecular drugs delivery and therapeutics [1].

The main constituents of biointerfaces (e.g., plasma and organelle membranes, alveolar surface, gastric mucosal barrier in the stomach wall, etc.) are biological surface-active molecules [2]. Major representatives among them, being self-assembled at the interface, are lipids and proteins. The lipids primarily provide the structural framework of the biological membrane, while the proteins carry out the biochemical processes that are specialized to membranes. Structural basis of any biological membrane is a lipid bilayer, a thin liquid film with few nanometer thickness, consisting of two phospholipid monolayers.

The artificially obtained model membrane systems either from synthetically produced or isolated from the cells phospholipids and proteins provide an excellent opportunity for the study the structure and function of biological membranes. Significant achievements in understanding the structure and function of membranes have been reached using the ideas, methodology and techniques of artificial membrane systems such as monolayers, bilayer and multilayer vesicles, Langmuir–Blodgett films, thin liquid films TLF (foam films and emulsion films), etc. Various properties of lipid bilayers have been obtained by TLF (bilayer lipid membranes, BLM), which bear close resemblance to those of biological membranes. Presenting inverse BLM, the foam TLF stabilized by lipids offer another possibility to

study the interactions between lipid monolayers [3–7]. An advantage of the model membranes is that commonly the system is more simple and well defined, and the results are easier for interpretation from the point of view of surface and colloid science.

Some main findings in the area of TLF in biological and medical science will be reviewed and discussed. A brief explanation of thin liquid films, their formation and stability will be followed by the main achievements in studies of films from phospholipid, protein and lipid–protein natural mixtures. Special attention will be devoted to TLF composed of pulmonary surfactant and its constituents at the air–liquid interface since, foam films offer new opportunities for studying the structure and stability of surfactant layer on the alveolar surface.

2. Thin liquid films

Since long time, thin liquid films (TLF) have been studied as they play an important role on stability of colloidal systems in liquid dispersion media. TLF form when two compartments of disperse phase (droplets, or bubbles or particles) come close to each other. Foam films, between two gas phases, and emulsion films, when liquid phase from which the film is formed is immiscible with the liquid of dispersed phase, are an example for symmetrical TLF while wetting films, thin liquid films separating a solid from a gas phase, are asymmetric (Fig. 1).

The most important factor which determines the properties of TLF is the interaction between the two film interfaces, as well as the interactions between the two adjacent phases across the liquid film. The thermodynamic quantity disjoining pressure Π is a result of these attractive or repulsive interactions due to different types of surface forces acting in the films. These forces can be grouped in at least four categories: (1) van derWaals forces, (2) electrostatic “double-layer” forces, (3) forces due to water structure such as repulsive hydration forces (also known as

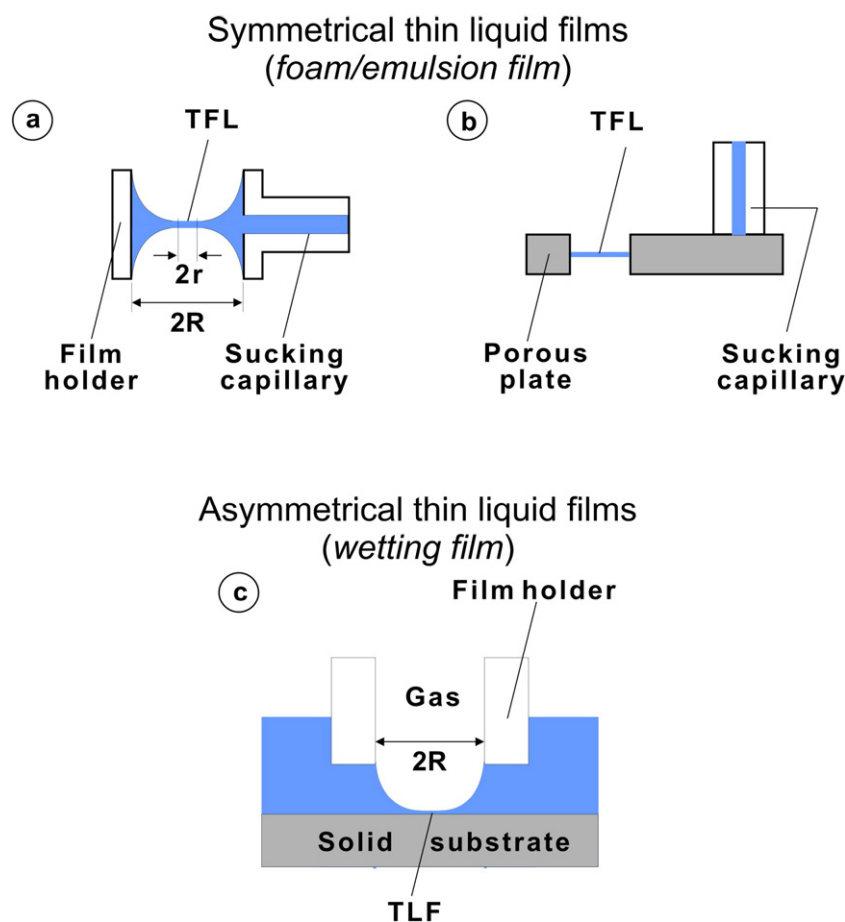


Fig. 1. Scheme of the measuring cells for the study of the TLF: (a and b) symmetrical films; (c) asymmetrical films. (Redrawn from [11].)

structural or solvation forces) and attractive hydrophobic forces and (4) steric–entropic forces, short- and long-range interactions, respectively, for small molecules and for macromolecules [5,8,9]. Two major categories of surface forces are usually distinguished: DLVO and non-DLVO surface forces [3^o,4,8]. The van derWaals surface force is attractive, while the double-layer force is repulsive. These two forces are presented between all colloidal particles in aqueous solutions, and they are described by the DLVO theory of Derjaguin, Landau, Verwey, and Overbeek [3^o,4,8,9]. However, the two DLVO forces, while always present, are not necessarily the only or even the prevalent interaction. At surface separations below about several molecular diameters, the non-DLVO forces can dominate over the DLVO forces. It is often difficult to distinguish between the different forces that control the interactions at short-range [8]. Hence, single TLF of all types are very useful models for the investigation of pair interactions (disjoining pressure, interaction energy, stability or instability, etc.).

Small circular foam (emulsion) films or wetting films, with a radius within the range of 10–500 μm , are considered as free-standing microscopic TLF (Fig. 1). An advantage over macroscopic TLF is the possibility of working at very low surfactant concentrations [3^o,4]. The measuring cell of Scheludko and Exerowa has proved to be a versatile and reliable tool for the formation of microscopic horizontal TLF at the constant capillary pressure (Fig. 1a). The film is formed in the middle of a biconcave drop. It thins after formation and a thick coloured film occurs. During the drainage process, black spots appear due to local fluctuation of the film thickness. These spots grow and finally cover the whole film. The very thin films appear black in reflected light and are called black films. Two types of black films exist. The thickness of the thicker common black film (CBF) and its stability is controlled by the electrostatic double-layer repulsion [3^o,7^o] in agreement with the classical DLVO

theory. A very thin Newton black film (NBF) is formed at equilibrium state when the electrostatic double-layer repulsion is suppressed, and the film thickness is only determined by short-range molecular interactions in adsorption layers.

In the cell of Exerowa–Scheludko (Fig. 1b), the microscopic TLF is formed in the cylindrical hole in a porous sinter-glass plate [3^o]. Porous plates of various pore radii can be used, which together with the surface tension of the solution, allows increase in the capillary pressure.

The microscopic wetting films on solid surface have been formed and studied in the experimental cell of Platikanov (Fig. 1c). The films are formed between the horizontal surface of the solid substrate and the hemispherical meniscus aqueous solution/air.

Using the microinterferometric method of Scheludko and Exerowa, the film lifetime τ , the probability of formation of black films W , the equilibrium film thickness h , the disjoining pressure Π and determining the $\Pi(h)$ isotherm can be measured [3^o,4,6^o].

The mechanism of TLF rupture, in the case of bilayer, due to fluctuations has been described by Kashchiev and Exerowa [3^o,6^o,10]. The theory defines equation for the main parameters describing the bilayer stability—the mean lifetime τ and the probability W for bilayer observation, which depend strongly on the bulk concentration (C) of the molecules in the film-forming solution. The mean lifetime can be presented as a function of C , as follows:

$$\tau = A(r) \exp[B / \ln(C_e/C)]$$

where $A(r)$ is connected with the hole nucleation kinetics, B is proportional to the work for hole formation in the film and C_e is the concentration of molecules at which the diluted and the condensed phase of vacancies in the film are in thermodynamic equilibrium.

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