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Wetting properties of model biological membranes

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ABSTRACT

Various aspects of native and model biological membrane wettability are discussed. Among others hydration of mono-, bi-, and multi-layers of lipids as well as wettability of macroscopic surfaces of solid supported lipid films was investigated via apparent contact angle measurements and calculation of the apparent surface free energy of the films. The effects of relative humidity on the layer hydration and contact angle changes are also discussed. Finally, the effect of liposomes and enzymes (due to the hydrolysis reactions) on the hydrophobic/hydrophilic character of the film surfaces is overviewed.

1. Introduction

Wetting phenomena are common and important in many industrial processes, accompanying everyday life, occurring in nature. One should mention several examples like flotation of minerals, oil recovery, lubrication, washing, painting, printing, gluing, corrosion protection, chemical plant protection, soil wetting, waste water treatment, etc. [1–7]. Let us first recall the definition of wetting process. Generally, wetting is the process when a fluid (liquid) displaces another fluid (gas or liquid) from a solid or immiscible liquid surface. This can be achieved by liquid spreading, immersion of a solid into a liquid, or contacting the two phases thus forming an adhesive joint. Moreover, processes can be preceded via adsorption of liquid vapors onto solid surface too [8]. Obviously, wetting processes are also important in native biological membranes. This paper is a review of the recent investigations of the wetting properties of model biological membranes.

Whether a given surface can be wetted or not by a liquid depends on the balance of cohesive forces in the liquid and adhesive forces operating at the solid/liquid interface. They can be of van der Waals nature (dispersion, dipole–dipole, dipole–induce dipole), electron-donor and electron-acceptor (including hydrogen bonding), π-electrons, and electrostatic interactions. In physical wetting no chemical bonds of solid/liquid are formed. If water is the wetting liquid, which most often takes place, solid surface can be classified as superhydrophilic, hydrophilic, hydrophobic and superhydrophobic. One can find suitable review articles published lately about fundamentals of wetting and charge effect [9] and discussion of hydrophobicity/hydrophilicity [10–12].

The commonly used parameter for wetting characterization is the '*wetting contact angle*' which can range between 0° to 180°. The contact angle is an angle between the solid surface and tangent to the liquid drop surface (the surface tension) measured across the liquid phase at the three-phase contact line in the solid/liquid drop/air system. It should be stressed that if a liquid completely spreads on a solid surface up to its film of molecular thickness, then there is no contact angle, and in the mathematical sense the contact angle is not equal to zero, because it would have a wrong implication in using the Young's equation [12]. Moreover, in the case of real solid surfaces, which are in most cases not ideal ones, the experimentally measured contact angle is an apparent one [13–15]. This is just the case for model biological layers discussed in this paper. Therefore, even if the term 'contact angle', will be used, it should be understood as an 'apparent contact angle'.

2. Two aspects of wetting of native biological membranes and their models

The wetting of biological membranes can be examined in two bearings. Namely, the first is that native biological cell membranes are surrounded by aqueous solutions and the cell interior cytoplasm can be also thought as a wetting phase. Water molecules, some ions, and substances are transported through the membrane into the interior. In this bearing, wetting of the membranes can be considered as their hydration. Numerous papers on this issue have been published [16–34]. The second bearing deals with wetting of the films of lipids (mostly phospholipids) deposited on a solid support (e.g. mica, silicon, glass, gold, and others), which apart from the issues of role of water in the

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native membranes, also some utilizable prospective is considered in the investigations, e.g. targeted drug delivery, biocompatible implants, biosensors, surfaces of design hydrophobic/hydrophilic surfaces, and others [4,5,35–47]. This paper is focused on the latter problem where wetting of macroscopic surface of the model films is studied by wetting contact angle measurements and surface free energy determination, although the former one is briefly discussed.

As mentioned above, the biomimetic systems used to study as models of native biological membranes are most often solid-supported lipid mono- and bilayers [48–52], suspended lipid bilayers, or supported vesicular layers [29,42,53–55], polymer-cushioned lipid bilayers [56], hybrid bilayers [57,58], and tethered lipid bilayers [59]. Several different procedures can be applied for their preparation: Langmuir–Blodgett or Langmuir–Schaefer techniques [25,26,36,43,45,47,60–62], spin-coating [42,53–55], and vesicle fusion [63–65]. Other methods for depositing supported lipid layers on both flat and textured surfaces are: adsorption of vesicles (liposomes) from an aqueous suspension and their subsequent fusion on the support surface [63,66–70], direct spreading from water or an organic solvent [22,36,41,44,71], spray-coating, dip-coating, and self-assembly. Preparation and investigation methods are described elsewhere [72,73].

3. Water hydrating model biological membranes

Water structure at the model mono-, bi- and multilayers of lipids has been intensively studied. Water presence is very essential for cell membrane functions although its structure and role are still not well known. A relatively recent review on the water/phospholipid interactions was published by Milhaud in 2004 [23,29,74]. Water molecules interact with lipid polar headgroups by relatively strong hydrogen bonds. It causes rupture of such bonding in the vicinal water. Milhaud [23] concluded that small water molecules can penetrate into free volumes of the layer and a specific hydration level can be assigned to each thermodynamical phase of the model membranes, where there is defined distribution of water molecules whose number trapped in the interbilayer spaces phospholipid/water determines the hydration state. This water is characterized by different hydrogen-bonded populations of water molecules. Increasing hydration of the lipid molecules causes swelling of their polar heads. The phospholipid–water equilibrium is governed by temperature and water activity. Hence if the pressure and temperature are constant, the relative humidity amount (RH) causes lyotropic transitions which may involve both interfacial (solvation transition) and hydrocarbon regions. However, besides the hydration water there are also "free" water molecules [23]. Pandit et al. [75] distinguish four regions of water which have different local densities at the lipid film. Depending on the state of the layer, its polar groups can adsorb ca. 11 (gel phase) or more than 20 (fluid phase) water molecules and spacing between the layers is similar to the water molecule size 0.29 nm, especially between the layers closer to the polar heads of 1,2-dipalmitoyl-*sn*-glycero-3-phosphocholine (DPPC) monolayer on mica. This was practically not found in the case of unsaturated 1,2-dioleoyl-*sn*-glycero-3-phosphocholine (DOPC) [21]. At the $-N(CH_3)$ choline group the water has the clathrate-like structure [20,76–78]. Then Berkowitz et al. [79] confirmed the density changes of the water vicinal to the DPPC layer surface. Also König et al. [30] found that 3–10 water molecules hydrated one the DPPC molecules, which corresponded to 8–20% water hydration, and this upper amount is the limit that can originate from air humidity. Moreover, Spangenberg et al. [22] observed (AFM) a significant rearrangement of DPPC layers on mica when exposed to water vapor at 40 °C. After 20 min small islands were formed, and after 30 min the lamellar structure with the expanded 5–6 nm thick terraces were observed. On the other hand, Benz et al. [80] observed a pronounced defect in DPPE (dipalmitoylophosphatidylethanolamine) monolayer immediately after its immersion in water.

Adsorption of water on the hydrophobic and hydrophilic DPPC films on the silicon substrate at low temperatures was investigated by Günster and Souda [25]. The hydrophilic DPPC bilayer was obtained by dipping the hydrophobic monolayer into the subphase. These adsorption experiments were conducted at low programmed temperatures ("closed-cycle He refrigerator") and in ultrahigh vacuum (base pressure 10^{-10} mbar). The temperature-programmed desorption spectroscopy was also applied. The water adsorption started in the temperature range 100–140 K. In the case of hydrophobic DPPC monolayer, the interactions were too weak for water molecule adsorption. Nevertheless, water molecules could interact with other water molecules settled on the surface thus forming clusters which were nuclei for condensation. This process was observed already at 106 K and surprisingly when the first water nuclei were formed the adsorption kinetics was similar on both hydrophobic and hydrophilic DPPC surfaces [25], which can be explained by the fact that both surfaces are terminated with $-CH_3$ groups. Different temperatures of the adsorption onset suggest that on the hydrophilic surface the attractive van der Waals interactions are stronger and hence the lifetime of water molecules is longer. Moreover, these studies showed that at any temperature applied, the hydrophobic DPPC surface is not wetted by water molecules. Quite the opposite, on the hydrophilic DPPC surface clearly visible coverage was found. If the coverage was less than a statistical water bilayer, i.e. $2 \cdot 10^{15}$ molecules per cm^2, small clusters were formed. The authors [25] concluded that even on the hydrophilic DPPC surface the adsorbed water molecules are not uniformly distributed due to anisotropic dipole–dipole interactions. The final stage corresponded to more than three water bilayers adsorbed. The desorption kinetic studies showed that on the hydrophobic DPPC surface individual water droplets were formed [25].

The results from AFM, near-field scanning optical microscopy (NSOM) and confocal microscopy have shown that the DPPC monolayer on freshly cleaved mica at RH up to 55% consisted of large liquid crystal (LC) islands surrounded by smaller ones and the liquid expanded (LE) domains. However, at a higher RH > 65% the small domains became mobile to coalesce, and then being less mobile they reached the critical size at RH > 85%. The RH dependent changes in the monolayer structure were natural evolution of the monolayer and no phase transition, and lipid removal or film collapse [34]. These observations were in agreement with those obtained earlier by others [81–85] and support our results of contact angle changes depending on the RH value which will be described later.

Surface properties of solid supported lipid layers strongly depend on the kind of the support and the method of the layer preparation and its thickness [29,41–47,86,87]. The layer surface can be hydrophobic or hydrophilic depending on the lipid polar head-group orientation at the surface/air interface, and the surrounding atmosphere and/or contacting phase.

Worth mentioning is the problem discussed in the literature earlier, which was called water 'vapor pressure paradox', i.e. different spacings between lipid layers deposited on a solid support (glass, mica) when exposed to the saturated water vapor (100% RH, less d-spacing) compared with those when contacting with liquid water [88]. However, Katsaras [87] using neutron diffraction has shown that DMPC multilayers adsorbed on mica which have the same spacing no matter whether they are immersed in water or contacted with saturated vapor, thus stating that there is no vapor pressure paradox. The earlier observed difference resulted from improper comparison of the experimental data dealing with the two systems. For example, the change in RH from 100% to 99.9% caused already ca. 0.5 nm decrease in the d-spacing.

4. Wetting of model biological membranes

4.1. Wetting of natural biological articular cartilage

The importance of wetting processes and interfacial free energy in native biological systems was investigated, among others, in the papers published by Pawlak et al. [5,6,38,39]. They consider articular cartilage