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Properties of Langmuir and solid supported lipid films with sphingomyelin

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ABSTRACT

Biological cell membranes play a crucial role in various biological processes and their functionality to some extent is determined by the hydrophilic/hydrophobic balance. A significant progress in understanding the membrane structure was the discovery of laterally segregated lipid domains, called the lipid rafts. These raft domains are of ordered lamellar liquid-crystalline phase, while rest of the membrane exists in a relatively disordered lamellar liquid-crystalline phase. Moreover, the chemical constitution of the lipid rafts consists of a higher content (up to 50%) of cholesterol (Chol) and sphingomyelin (SM). Sphingomyelin also plays a significant role in the red cells of blood and nerves, in some diseases, as a precursor to ceramides, and other sphingolipid metabolites.

In this paper properties of Langmuir and solid supported mixed lipid films of DPPC/SM, DOPC/SM, and Chol/SM are described. Special attention has been paid to wetting properties (hydrophobic/hydrophilic balance) of these films transferred onto a hydrophilic glass surface. To our knowledge such results have not yet been published in the literature. The properties were determined via contact angle measurements and then calculation of the films' apparent surface free energy. The films' wettability and their apparent surface free energy strongly depend on their composition. The energy is affected by both the structure of hydrocarbon chains of glycerophospholipids (DPPC and DOPC) and their interactions with SM. Properties of mixed Chol/SM monolayer depend also on the film stoichiometry. At a low Chol content (XChol = 0.25) the interactions between SM and Chol are strong and hence the formation of binary complex is possible. This is accompanied by a decrease in the film surface free energy in comparison to that of pure SM monolayer, contrary to a higher Chol content where the monolayer energy increases. This suggests that cholesterol is excluded from the membrane thus increasing the film hydrophilicity. These results are consistent with the literature data and somehow confirm the hypothesis of lipid raft formation. The roughness of the investigated monolayer surfaces was also determined using optical profilometry. The roughness parameters of the DPPC, SM, and mixed DPPC/SM generally correlate with the changes of their apparent surface free energy, i.e. with the decreasing roughness the apparent surface free energy also decreases. However, this is not the case for mixed DOPC/SM monolayers. Although the roughness increases with SM content the apparent surface free energy decreases. Therefore some other factors, like the presence of unsaturated bonds in the DOPC molecule, influence the film phase state and the energy too. More experiments are needed to explain this hypothesis.

Contents

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1. Introduction

1.1. Biological cell membranes

It is well known that membranes play an essential role in various biological processes, such as communication, cell interactions, signal transduction, active transport, as well activity of various hormones, drugs, and other molecules that occur on membranes [1–6]. Therefore a lot of effort is being put into studying cell membrane properties. Nevertheless, the studies on dynamics, structure and interactions in natural biological membranes still remain a very challenging subject. The biological membrane, in a simplified way, is defined as a specific assembly of lipids responsible for various biological functions in the cell. This assembly refers to the bilayer built up of lipids and being a basic structural unit of the cell membrane. In fact, the structure of native biological membranes is rather complex and heterogeneous. For example, the mammalian cell membranes are composed of an array of sterols, glycerophospholipids and sphingolipids that vary in head-group and acyl-chain composition [4,7]. In a given cell type membrane phospholipids may amount to more than a thousand molecular species [8]. Moreover, the membranes differ not only in the amount of respective lipid species but also in the distribution between the inner and outer leaflet of the bilayer [9]. The complexity of lipid structures is revealed from their diverse roles in membrane dynamics, protein regulation, signal transduction and secretion [10]. For this reason, to evaluate the features and interactions taking place in native biological membranes, researchers create various simplified, artificial models having specified lipid composition and content. These model systems are designed to mimic the properties of natural membranes and simultaneously to allow their precise examination. Among the most frequently applied model systems one can distinguish liposomes, black lipid membranes, Langmuir films, solid-supported lipid membranes, hybrid and polymer cushioned lipid bilayers [4,11–29].

The biological membrane possesses some fluidity which results from the temperature dependent motion of lipids and proteins. Studies on the diversity of membrane lipids and proteins revealed that those components have a unique ability to create “aggregates” [30]. In recent years researchers have found various restrictions of the membrane component movement, which may lead to formation of domains in the membrane [30]. The membrane domains are considered to be fragments having different lipid and protein composition than the rest of the membrane plane [31,32].

1.2. Rafts as lipid domains in the membranes

An exciting novelty in the field of membrane biology has been the hypothesis that plasma membranes may contain laterally segregated lipid domains known as the lipid rafts [33–37]. These discrete lipid raft domains are postulated to exist in a relatively ordered lamellar liquid-crystalline phase (L_o), whereas non-raft regions of the membrane exist in a relatively disordered lamellar liquid-crystalline phase (L_d), which means that lipids in domains have a tendency to occur in less fluid state than lipids in the surrounding biological membrane [35]. Although a key evidence for the existence of the lipid rafts has been the isolation of detergent-resistance membrane fractions from human and animal cells, the biophysical demonstration of coexistence of L_o and L_d phase in the model lipid membranes supported this hypothesis and provoked a series of studies. The general definition of lipid rafts has been approved, and specifies them as small, heterogeneous, highly dynamic, sterol and sphingolipid enriched domains, that compartmentalize cellular processes [37,38]. Knowledge of lipid raft properties and composition is very important from the point of view of their role in human physiology and pathogenesis of different diseases [39]. According to some data, the lipid rafts assist numerous signaling of proteins and receptors facilitating their functioning [40,41]. There is an evidence that rafts are sites for the binding and transport into the cell of several pathogens and toxins, including human immunodeficiency virus 1 (HIV-1) and the prion protein PrP^{SC} [40,42,43]. They are also considered to play a crucial role in dementing diseases such as Alzheimer's, Parkinson's, amyotrophic lateral sclerosis, Huntington's [41,44].

A typical chemical constitution of lipid rafts is related to a higher content of cholesterol and sphingomyelin [45]. Their concentration in rafts is about 50% higher than in the residual part of biological membrane. Studies on the lipid rafts content have revealed also that most of the phospholipids present in rafts contain at least one unsaturated hydrocarbon chain [46]. The canonical composition of the lipid rafts in the model lipid membranes studies is an equimolar mixture of phosphatidylcholine, sphingomyelin and cholesterol [34]. This proportion in a model membrane allows to present of two separated fragments existing in the L_o and L_d phase [30,35]. The role of cholesterol in regulation of fluidity in biological membranes and formation of microdomains is well known and thoroughly studied [47,48]. Therefore a lot of attention is paid to study the effect of this compound on other membrane lipids. Investigations of model systems of cholesterol and phosphatidylcholines having different structures of their polar head and chain saturation, or ternary mixtures composed of phospholipids, sphingolipids, and cholesterol, provide information on lateral organization of the lipids, tendency to formation of liquid ordered phase, phase separation, structure of the domains, and the ability of sterol to close packing with lipids [7,9,17,42,49–60]. The systems composed of cholesterol and lipids equivalent to native external membrane leaflet have been investigated by many authors using liposomes or vesicles [15,53–56,58], the Langmuir films [16–19,61–64], and supported lipid membranes [19,23,65,66].

1.3. Sphingomyelin in cell membranes

Sphingomeylin belongs to sphingolipids having the phosphorylated choline head group [7,10]. Especially its large amount is present in the membranes of nerve cells and blood red cells [67]. Its abnormally accumulated concentration in lysosomes has been found in the case of

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