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Lateral diffusion in equimolar mixtures of natural sphingomyelins with dioleoylphosphatidylcholine

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Abstract

Cellular membranes of mammals are composed of a complex assembly of diverse phospholipids. Sphingomyelin (SM) and phosphatidylcholine (PC) are important lipids of eukaryotic cellular membranes and neuronal tissues, and presumably participate in the formation of membrane domains, known as “rafts,” through intermolecular interaction and lateral microphase decomposition. In these two-dimensional membrane systems, lateral diffusion of lipids is an essential dynamic factor, which might even be indicative of lipid phase separation process. Here, we used pulsed field gradient nuclear magnetic resonance to study lateral diffusion of lipid components in macroscopically oriented bilayers composed of equimolar mixtures of natural SMs of egg yolk, bovine brain, bovine milk and dipalmitoylphosphatidylcholine (DPPC) with dioleoylphosphatidylcholine (DOPC). In addition, differential scanning calorimetry was used as a complementary technique to characterize the phase state of the lipid bilayers. In fully liquid bilayers, the lateral diffusion coefficients in both DOPC/DPPC and DOPC/SM systems exhibit mean values of the pure bilayers. For DOPC/SM bilayer system, this behavior can be explained by a model where most SM molecules form short-lived lateral domains with preferential SM–SM interactions occurring within them. However, for bilayers in the presence of their low-temperature gel phase, lateral diffusion becomes complicated and cannot simply be understood solely by a simple change in the liquid phase decomposition.

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1. Introduction

Cellular membranes of mammals are composed of a complex group of various phospholipids. There, sphingomyelin (SM) and phosphatidylcholine (PC) are among the major classes of lipids present in cellular plasma membranes. PC has a glycerol backbone with C3 hydroxyl esterified to phosphocholine and hydroxyls C1 and C2 esterified to fatty acids (Fig. 1). Most of the natural SMs also have the phosphocholine head group connected to the hydroxyl group on carbon one of a long-chain base and have a long, highly saturated acyl chain linked to the amide group on carbon two of the long-chain base [1]. Differences in the molecular structures of SM and PC lead to dissimilarity in their

intermolecular interactions, especially with respect to cholesterol (CHOL), an important constituent of eucaryotic cell membranes [2]. This difference in interaction may result in the formation of SM- and CHOL-rich domains, or “rafts,” which are believed to be important in cellular processes such as signal transduction, protein and lipid transport, and sorting [3]. Thus, properties of bilayers composed of mixtures of SM and PC are of specific interest.

Naturally occurring SMs are complex in composition [4,5]. They include dozens of molecular species with two types of long-base chains, sphingosine and sphinganine, which vary widely in length and degree of unsaturation. The content of SMs influences the bilayer’s physical properties, including lateral diffusion [6–9] and formation of ordered domains in bilayers [10]. Lipid bilayers containing PC and SMs have been studied by calorimetry [11–14], X-ray diffraction [8,11,12] and to some extent by pulsed field gradient nuclear magnetic resonance (pfg NMR) [15,16].

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