

# The influence of headgroup structure and fatty acyl chain saturation of phospholipids on monolayer behavior: a comparative rheological study

Nicolas Anton<sup>a,b</sup>, Patrick Saulnier<sup>a,b,\*</sup>, Frank Boury<sup>a,b</sup>, Françoise Foussard<sup>c</sup>, Jean-Pierre Benoit<sup>a,b,d</sup>, Jacques E. Proust<sup>a,b</sup>

<sup>a</sup> *Inserm U646, Ingénierie de la Vectorisation Particulaire, 10 rue A. Boquel, F-49100 Angers, France*

<sup>b</sup> *University of Angers, F-49100 Angers, France*

<sup>c</sup> *Laboratoire de Biochimie, Faculté de Pharmacie, 16 bd Daviers, F-49100 Angers, France*

<sup>d</sup> *École Pratique des Hautes Études (EPHE), 12 rue Cuvier, F-75005 Paris, France*

Received 20 December 2006; received in revised form 4 June 2007; accepted 4 June 2007

Available online 14 July 2007

## Abstract

This paper compares six phospholipidic monolayers at the water/chloroform interface by performing dilational rheological measurements with a drop tensiometer apparatus. The chosen lipids differ both in their headgroup structure and fatty acyl chain saturation or symmetry. The study concentrated on monolayers formed with DPPC, DPPE, DOPC, DOPE, POPC and POPE. Using a generalized Maxwell rheological model, transposed at the interface, the intimate intermolecular interactions between amphiphilic molecules are studied on and off the monolayer plane. The equilibrium and nonequilibrium phenomena are analyzed and, respectively, correlated with monolayer cohesion and with monolayer/sub-surface interactions. The purpose of this work is to gain further insights into the influences (as slight as they are) of the weak changes in phospholipid structure and on the behavior of the monolayers. The results, widely described, provide further details on nuances existing between very similar molecules, and likewise, on the synergies created between the different effects.

© 2007 Elsevier Ireland Ltd. All rights reserved.

**Keywords:** DPPE; DPPC; DOPE; DOPC; POPE; POPC; Interfacial rheology; Dilational rheology

## 1. Introduction

Research focused on the self-assembly of phospholipids has proved to be of crucial importance in the study of many biological processes as well as in other medical, pharmaceutical and industrial applications. Overall, these phenomena are governed by the thermodynamic and physicochemical parameters of the bilayers, reflected by the cohesion of the layer related to in-plane order and disorder, by the hydration state of the headgroups, and even by the relative out-of-plane interactions

\* Corresponding author at: Inserm U646, Ingénierie de la Vectorisation Particulaire, 10 rue A. Boquel, F-49100 Angers, France.

*E-mail addresses:* [nicolas.anton@univ-angers.fr](mailto:nicolas.anton@univ-angers.fr) (N. Anton), [patrick.saulnier@univ-angers.fr](mailto:patrick.saulnier@univ-angers.fr) (P. Saulnier), [frank.boury@univ-angers.fr](mailto:frank.boury@univ-angers.fr) (F. Boury), [francoise.foussard@univ-angers.fr](mailto:francoise.foussard@univ-angers.fr) (F. Foussard), [jean-pierre.benoit@univ-angers.fr](mailto:jean-pierre.benoit@univ-angers.fr) (J.-P. Benoit), [jacques.proust@univ-angers.fr](mailto:jacques.proust@univ-angers.fr) (J.E. Proust).

of the amphiphile sub-surface. Furthermore, some models of lipid bilayers have been shown to be successful for fitting natural systems, and thus disclosing intimate interactions between phospholipidic amphiphiles within the membrane. A number of studies have been focused on the phase behavior of the binary lipid/water system and on the particular study of the  $L_{\alpha}$  liquid crystalline phases, since amphiphilic mobility is comparable to that of biological membranes (Janiak et al., 1979). Besides, much research has studied simple lipid monolayers at the air/water interface, the so-called Langmuir monolayers, for their features of being *fully hydrated systems*, which resides on a semi-infinite reservoir of water much closer to the conditions of biomembranes than of partially dehydrated systems (Möhwald, 1993; Lui et al., 1994; Evans, 1995; Romao and Gonçalves da Silva, 2004; Garidel and Blume, 2005; Dyck et al., 2005; Korchowicz et al., 2006). The usual experimental methods for studying such monolayers in great detail include optical techniques such as fluorescence microscopy, fluorescence spectroscopy and ellipsometry, etc., and X-ray or neutron scattering (Möhwald, 1993). Phospholipid monolayers spreading at the oil/water interface have also been widely studied (Brooks and Pethica, 1964, 1965), the surface pressure ( $\pi$ ) being considerably higher with regard to the air/water interface. The cohesive interactions between lipid chains are reduced and the model of a biological membrane becomes more apparent.

In this study we focused, at the oil/water interface, on six different pure (i.e. one-component) phospholipid monolayers, made with molecules differing in their headgroup structures (PE and PC), in acyl chain saturation (DP and DO) and even in acyl chain symmetry (PO). Explicitly we used: DPPC, DPPE, DOPC, DOPE, POPC and POPE. The purpose was to gain further insights into the influence of weak structural variants of the amphiphile structure on the monolayer features and in-plane and out-of-plane intermolecular interactions as enumerated above. The monolayers were formed by the gradual adsorption of the surfactant at the chloroform/water interface of the pendant water drop, in a drop tensiometer apparatus. As a mechanical approach for studying such characteristics of lipid monolayers, we performed comparative dilational rheological experiments (Kretzschmar et al., 1996; Li et al., 1996a,b, 1999; Miller et al., 1998; Wüstneck et al., 2002a,b; Roberts et al., 2005) analyzed with a rheological model, based on the volumic generalized Maxwell model transposed at the interface (Saulnier et al., 2001).

## 2. Materials and methods

### 2.1. Materials

Dipalmitoylphosphatidylethanolamine (DPPE), dipalmitoylphosphatidylcholine (DPPC), dioleoylphosphatidylethanolamine (DOPE), dioleoylphosphatidylcholine (DOPC), 2-oleoyl-1-palmitoylphosphatidylethanolamine (POPE) and 2-oleoyl-1-palmitoylphosphatidylcholine (POPC) obtained from Sigma were used. These lipids were dissolved in chloroform/methanol (3:1), HPLC grade, purchased from Prolabo (Fontenay-sous-Bois, France). This first dissolution is performed to obtain a phospholipid concentration of  $\sim 6$  mM, and a second dilution in pure chloroform that gives a concentration of  $\sim 0.02$  mM. Ultrapure<sup>®</sup> water was obtained with the MilliQ filtration system (Millipore, Saint-Quentin-en-Yvelines, France). Moreover, considering the low solubility of chloroform in water, they were previously mixed and saturated for about 1 week. The lipid concentration was chosen to correspond to the critical micelle concentration in the organic phase (which is mostly chloroform; for both instances, see Li et al., 1996a), forming an inverse micellar suspension. This method insured both the complete saturation of the water/organic interface, and the stable features of the forming monolayer in the bulk phases (an important detail for the rheological study).

### 2.2. Methods

#### 2.2.1. Drop tensiometer

Rheological measurements were performed with a drop tensiometer device (Tracker Teclis, Longessaigne, France). The (instantaneous) axisymmetric shape of a drop, pendant or rising, is analyzed at constant temperature to provide the surface tension value. In our case, the drop is a pendant drop of water in the organic phase, which contains the phospholipids. The temperature was maintained at  $(21 \pm 2)^\circ\text{C}$ , and the measurements were performed three times. Each rheological experiment was performed at equilibrium, after the complete saturation of the water/chloroform interface. The first stage, prior to rheological experiments, is the formation of the monolayer by the gradual diffusion of the amphiphiles at the interface until complete saturation is achieved. Throughout the adsorption kinetics, the drop area is maintained constant in order to create a direct link between molecule adsorption and the surface tension; saturation is reached when the tension stabilizes. The kinetics appears relatively fast, these being consistent with the literature for similar systems at the water/chloroform interface (Li et

Download English Version:

<https://daneshyari.com/en/article/1253727>

Download Persian Version:

<https://daneshyari.com/article/1253727>

[Daneshyari.com](https://daneshyari.com)