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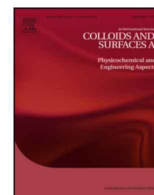

Phospholipid adsorption at oil in water versus water in oil interfaces: Implications for interfacial densities and bulk solubilities

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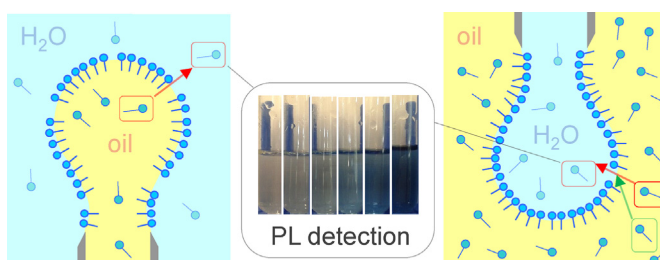
HIGHLIGHTS

- Comparison of an oil drop in water and a water drop in oil.
- Phospholipids (PL) adsorb at the interface, but also enter the water phase.
- Concentration of PL in the oil drop decreases by dissolution in water.
- The loss of PL from the oil is negligible for a water drop in oil.
- More precise interfacial tension vs. PL concentration for water drops in oil.

GRAPHICAL ABSTRACT



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ABSTRACT

The adsorption of the phospholipid (PL) 1,2-dipalmitoyl-sn-glycero-3-phosphocholine (DPPC) dissolved in the oil phase squalene or squalane was studied at the interface with water. Dynamic interfacial tension was measured by profile analysis tensiometry (PAT). Two different setups were considered, a buoyant oil drop surrounded by water or a pendant water drop in oil. For the proof of methodology the interfacial tensions of water in chloroform and chloroform in water interfaces were measured. From the equilibrium interfacial tensions of different PL concentrations, the Gibbs adsorption isotherm was determined. These isotherms allow the extraction of the minimal areas per lipid molecule as well as critical aggregation concentration (CAC). We found significant differences in the results obtained for both setups. By means of PAT, the CAC determined for water drops in oil was smaller than for oil drops in water. Photon correlation spectroscopy (PCS) and nuclear magnetic resonance (NMR) were used to verify the determined CACs. We concluded the setup-dependent differences to be caused by depletion effects when initially dissolving the surface active component in the small drop volume. We recommend the reversed setup where the surface active component is dissolved in the surrounding bulk phase to avoid corrections of bulk concentrations.
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1. Introduction

The adsorption kinetics of phospholipids (PLs) is described extensively at the air/water surface [1]. Development of profile analysis tensiometry (PAT) then gave rise to studies of the interfaces between water and an immiscible organic phase like chloroform/water [2,3], n-dodecane/water [4] and triolein/water

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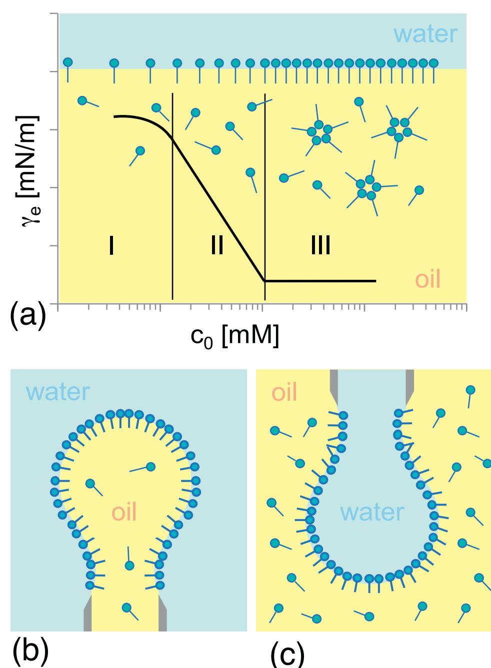

Fig. 1. Schematic illustration of the adsorption isotherm and the two different PAT measurement setups. (a) 3 regimes of PL solubility were distinguished: I-molecular dissolved PLs below CAC, II-PLs adsorb at the interface until a full coverage is reached at CAC, III-PLs start to aggregate and form micelles above CAC. Two setups at the tip of a capillary: (b) PL-containing phase inside the buoyant oil drop; (c) PL-containing phase outside of the pendant water drop.

[5]. Measurement of dynamic interfacial tension with PAT is an established and well-described method for the characterization of liquid interfaces [4]. By investigating the adsorption of surfactants as a function of time and concentration, this non-invasive method provides information about the surfactants dynamic behavior during formation of an interfacial layer and its convergence toward thermodynamic equilibrium. The course of dissolution in the bulk and adsorbing behavior at the interface can be separated into three regimes-an initial, adsorbing and saturated state. This is intensively discussed for self-organizing surfactants at air/water interfaces forming micelles in the aqueous bulk [6,7] or reversed micelles in non-polar solvents [8] and also drawn in Fig. 1a. By analyzing adsorption isotherms of PLs between immiscible phases, the critical aggregation concentration (CAC) can be obtained. It reveals solubility limits of the lipids in the organic phase, equivalent to the critical micelle concentration (CMC) for surfactants in aqueous systems [2]. Additionally, the minimal interfacial area per lipid molecule can be calculated in order to determine interfacial packing densities of the molecules. A comparison of phospholipid monolayers at the air/water and the oil/water (O/W) interfaces was provided by Grandell and Murtomäki [9].

For the formation of a PL monolayer at the interface between two immiscible liquids, it is theoretically not relevant for their equilibrium state from which side the PLs enter the interface. Usually the liquid phase chosen as solvent for the PLs is the one having the higher solubility for the PLs depending on their respective hydrophilic-lipophilic balance (HLB) value [10,11]. Measurements by PAT were generally performed for the PL-containing phase inside the droplet [2–5,9,12] as is illustrated in Fig. 1b.

In the current study, measurements in a reversed setup (shown in Fig. 1c) were accomplished, where the PL-containig phase was located around a water phase. The measurements at the water/oil (W/O) interface revealed differences in the results for the adsorption isotherms compared to those obtained with the common setup. These differences, especially in CAC, were caused by the transfer of phospholipids from the limited drop volume into the surrounding water phase. These effects were investigated additionally in separate experiments. The transfer of phospholipids from oil to water phase was tested experimentally, using a phosphorus quantification assay of the aqueous phase. The discrepancies between the O/W and W/O adsorption processes were analysed by the PAT technique and interpreted under consideration of the PL phase transfer. Additionally, data from photon correlation spectroscopy (PCS) and nuclear magnetic resonance (NMR) diffusometry were carried out and these data were interpreted in order to determine the precise CAC.

2. Experimental

2.1. Materials

The DPPC was purchased from Lipoid (Ludwigshafen, Germany). The lipid was received as a powder and dissolved in either chloroform or in an oil phase depending on the experimental set-up of the PAT instrument. Squalene with a purity of ≥98% and its hydrogenated form squalane with a purity of >99% were obtained from Sigma–Aldrich (Taufkirchen, Germany) and used as oil phases. As an additional organic phase, trichloromethane with a purity of >99.8% was acquired from Merck (Darmstadt, Germany). Considering the low solubility of chloroform ($CHCl_3$) in water, the chloroform aliquot used for the experiments was saturated with water in advance for about 3 days at the minimum. Highly purified water was purchased from VWR International (Darmstadt, Germany). To investigate the diffusion coefficient of DPPC in chloroform with NMR, deuterated chloroform ($CDCl_3$) with a purity of 99.95% was obtained from Deutero (Kastellaun, Germany). For phosphorus quantification the reducer, ammonium molybdate, and perchloric acid (30%), were purchased from Sigma–Aldrich (Taufkirchen, Germany). Sulphuric acid, with a purity of 95–98%, and KH_2PO_4 were obtained from Merck (Darmstadt, Germany).

2.2. Method

2.2.1. Preparation of the oil phase and PCS

The oil phase was prepared by dissolving 0.1 mM–10 mM DPPC in squalene or squalane with energy input. Briefly, the oil/DPPC mixture was placed in an ultrasonic water bath Sonorex RK 514 Transistor from Bandelin electronics (Berlin, Germany) for a minimum of 2 h until complete dissolution of lipids was achieved. Dissolution of the initial PL aggregates was monitored by measuring the reduction of size using dynamic light scattering.

For PCS, the Zetasizer Nano ZS90 from Malvern Instruments (Worcestershire, UK) was used. Before each measurement the oil sample was temperated 5 min at 20 °C in a cuvette in the PCS device. Then 3 measurements were carried out, with the number of runs depending on the amount of particles detected in the sample. If <10 particles were detected by light scattering, the number of runs was set to 100. The average particle size, the polydispersity index (PDI), and the count rate were determined. The sample was exposed to ultrasonication until the dissolution of PL was completed, i.e., when the size and number of detected particles were in the range of those of the pure oil phase or chloroform, respectively. Mean particle sizes (Z-average) ≤30 nm and a derived count rate (DCR) ≤ 5 kilo counts per second (kcps) were defined as quality cut-off values as was already shown exemplarily with squalene [13]. For the evaluation of the CAC, different concentrations of DPPC were tested additionally, to prove full solubility or existence of aggregates. For this, the prepared stock solution was diluted several times and each diluted

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