



Cation effects on phosphatidic acid monolayers at various pH conditions



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ABSTRACT

The impact of pH and cations on phase behavior, stability, and surface morphology for dipalmitoylphosphatidic acid (DPPA) monolayers was investigated. At pH < 10, DPPA monolayers on water are predominantly populated by neutral species and display the highest packing density. Cations are found to expand and stabilize the monolayer in the following order of increasing magnitude at pH 5.6: Na⁺ > K⁺ ~ Mg²⁺ > Ca²⁺. Additionally, cation complexation is tied to the pH and protonation state of DPPA, which are the primary factors controlling the monolayer surface behavior. The binding affinity of cations to the headgroup and thus deprotonation capability of the cation, ranked in the order of Ca²⁺ > Mg²⁺ > Na⁺ > K⁺, is found to be well explained by the law of matching water affinities. Nucleation of surface 3D lipid structures is observed from Ca²⁺, Mg²⁺, and Na⁺, but not from K⁺, consistent with the lowest binding affinity of K⁺. Unraveling cation and pH effects on DPPA monolayers is useful in further understanding the surface properties of complex systems such as organic-coated marine aerosols where organic films are directly influenced by the pH and ionic composition of the underlying aqueous phase.

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1. Introduction

Phosphatidic acid (PA) is crucial for the maintenance of cell membranes. Although it exists in small amounts (~1%) due to its high turnover rate (Munnik, 2010), PA is a key metabolite in the synthesis and breakdown of larger membrane phospholipids in addition to participating in other important cellular functions, e.g., vesicle fission and fusion, cell signaling, and protein binding (Athenstaedt and Daum, 1999; Eaton et al., 2014; Kooijman et al., 2003; Kooijman and Testerink, 2010; Wang et al., 2006). Besides being a minor phospholipid in the cell membranes of mammals and plants, PA is also known to be widely distributed among different species of marine microorganisms (Ackman, 1989).

Phospholipids from the marine biota such as dipalmitoylphosphatidic acid (DPPA) and dipalmitoylphosphatidylcholine (DPPC) are believed to be important sources of saturated fatty acids found in the sea surface microlayer (SSML) and at the surface of marine aerosols (Lee et al., 2007; Marty et al., 1979; Tervahattu et al., 2002). In particular, saturated fatty acids with 16 (palmitic acid) and 18 (stearic acid) carbon alkyl chains are known to be the most abundant. These surface-active organic compounds ultimately

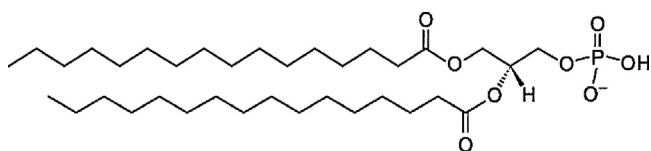
form thin films that affect aerosol growth and volatility, radiative absorption and scattering, reactivity with atmospheric gases, and cloud condensation nuclei activity (Andrews and Larson, 1993; Beaver et al., 2010; Burrows et al., 2014; Clifford et al., 2007; Glass et al., 2006; Moroi et al., 2004; Reeser et al., 2013). In turn, the interfacial properties of these films are directly influenced by the pH and ionic composition of the aqueous phase.

Interestingly, such complexity is generally not modeled in current atmospheric simulations as primary organic aerosols are still treated as uniform, and differences in aerosol size and hygroscopicity due to organic matter are typically neglected (Burrows et al., 2014). As marine aerosols have regional distributions of ions and organic matter that can be distinctly different (Ault et al., 2013; Millero et al., 2008), they will have, as stated by Elliott et al. (2014): “[...] different critical organic parameters not limited to interfacial coverage, the two dimensional phase state, chemically dependent hygroscopicities, mass to carbon ratio and even density”. Thus understanding the surface properties of model organic films with environmentally-relevant ions at air-aqueous interfaces will help to improve atmospheric aerosol climate modeling.

In that regard, DPPA monolayers can be useful and relevant proxy systems for the SSML and organic coatings on marine aerosol surfaces (Lin et al., 2015). Moreover, DPPA constitutes a simple enough lipid model (Scheme 1) for studying the effects of ions on

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Scheme 1. Chemical structure of (singly protonated) DPPA.

lipid surface behavior and morphology including alkyl chain conformation, hydration state, and ion interactions with the phosphate headgroup at air-aqueous interfaces (Tang and Allen, 2009; Tang et al., 2011; Tang et al., 2010). Previous studies have shown that DPPA monolayers are impacted by the pH, ionic composition, and hydrogen bonding of the underlying aqueous solution, all of which affect the ionization state of DPPA's phosphate headgroup (Kim et al., 1996; McNamee et al., 2011; Miñones Jr et al., 2002; Papahadjopoulos, 1968; Patil et al., 1979). For example others have previously examined the surface phase behavior of DPPA monolayers on water and shown how it is affected by different pH and temperature conditions (Miñones Jr et al., 2002). However, the influence of solution ionic composition and DPPA headgroup-ion complexation has yet to be fully elucidated.

In this work, we examine the effects of pH and marine-relevant cations (Na^+ , K^+ , Ca^{2+} , and Mg^{2+}) on DPPA's phase behavior, stability, and surface morphology using surface pressure-area isotherms and Brewster angle microscopy. The investigation of these properties is particularly applicable to marine aerosol surfaces, where enrichment of specific cations may impact the surface morphology and organization of organic films (Ault et al., 2013; Millero et al., 2008).

2. Materials and methods

2.1. Materials

1,2-Dipalmitoyl-*sn*-glycero-3-phosphate (DPPA) monosodium salt (>99%, lyophilized powder) was purchased from Avanti Polar Lipids (Alabaster, AL; M_w 670.873 g/mol). The average molecular weight (M_w) is 670.455 g/mol due to the variability in the Na^+ content. NaCl , KCl , MgCl_2 , and CaCl_2 salts (>99%, ACS certified) were purchased from Fisher Scientific (Waltham, MA). Chloroform and methanol (HPLC grade) as well as trace metal grade HCl and NaOH were also from Fisher Scientific. Ultrapure water with a resistivity of 18.2 $\text{M}\Omega\text{ cm}$ and a measured pH of 5–6 (the water pH is slightly acidic due to dissolved atmospheric CO_2) was obtained from a Barnstead Nanopure filtration system (D4741, Thermolyne Corporation, Dubuque, IA) equipped with additional organic removing cartridges (D5026 Type I ORGANIC-free Cartridge Kit; Pretreat Feed).

2.2. Preparation of lipid and salt solutions

DPPA stock solutions were prepared by dissolution in a 7:3 (v/v) chloroform:methanol mixture. All aqueous salt solutions were prepared at 0.6 M by dissolution in pure water. Salts and salt solutions were pretreated according to previously reported procedures to minimize the impact of organic contamination (Hua et al., 2013). NaCl and KCl salts were baked at 650 °C, whereas MgCl_2 and CaCl_2 solutions were filtered at least thrice using activated carbon filters (Whatman Carbon-Cap 75, Fisher Scientific) to remove organic contaminants. A separate set of carbon filters was used for each salt to avoid any ion cross-contamination. The significance of organic contamination and the need to treat salts cannot be understated and is discussed in the Supporting

information (see Fig. S1). The concentration of these purified stock solutions was determined by Mohr's chloride titration method (Finlayson, 1992). Each solution was prepared by serial dilutions of the purified stock solutions. The pH of the prepared solutions was adjusted by adding the required amounts of stock concentrated HCl and 10 M NaOH.

2.3. Compression isotherm measurements

Surface pressure-molecular area (Π - A) compression isotherms of DPPA monolayers on neat water and salt solutions were obtained using a computer-controlled Langmuir trough (Mini-trough, Biolin Scientific USA, Paramus, NJ). The trough is made of Teflon and has dimensions of 168 mm \times 85 mm. The monolayer is symmetrically compressed using two Delrin-coated barriers. Surface pressure was measured during compression by the Wilhelmy plate method. Filter paper (Ashless grade, Whatman) was used as Wilhelmy plates. Prior to each experiment, the presence of extraneous surface-active contaminants was checked by sweeping the surface of the aqueous solution with the barriers until no significant change in the surface pressure (<0.1 mN/m) was observed. A measured amount of DPPA was spread dropwise onto the aqueous surface using a glass microsyringe (1725RN, Hamilton, Reno, NV). After spreading, solvent evaporation was allowed for approximately 10 min. The barriers were compressed at a rate of 5 mm/min/barrier. Isotherms were also tested at 10 and 15 mm/min/barrier compression rates with no observable differences found. All experiments were performed at room temperature (21 ± 1.5 °C) and atmospheric pressure and humidity. Isotherms were repeated in sets of triplicates, with a maximum allowed error of $\pm 0.25 \text{ \AA}^2$ (see Fig. S2 in the Supporting information). A maximum difference of $\pm 0.5 \text{ \AA}^2$ exists between sets due to small daily fluctuations in temperature.

2.3.1. Brewster angle microscopy (BAM) imaging

BAM images were collected simultaneously with the compression isotherms on a custom-built BAM setup described previously (Adams and Allen, 2013; Griffith et al., 2012). The laser source (Research Electro-Optics, Boulder, CO) emits 5 mW *p*-polarized light at 543 nm. The output laser beam is first attenuated by a half-wave plate (Ekspla, Lithuania) then filtered by a Glan polarizer (Ekspla, diameter 14 mm) before reaching the aqueous surface at the Brewster angle (53.1° on water; this value was slightly adjusted for the various salt solutions). The reflected beam is collected by a $10 \times$ infinity-corrected super-long working distance objective lens (CFI60 TU Plan EPI, Nikon Instruments, Melville, NY; NA 0.21) and collimated by a tube lens (MXA22018, Nikon Instruments; focal length 200 mm) onto a back-illuminated EM-CCD camera (iXon DV887-BV, Andor Technology USA, Concord, MA; 512×512 active pixels with $16 \mu\text{m} \times 16 \mu\text{m}$ pixel size). Because the inclined position of the imaging optics results in only a narrow region of the image being well focused, final images were cropped down from their full size ($800 \mu\text{m} \times 800 \mu\text{m}$) to show the most resolved region. The lateral resolution of the BAM images was $\sim 1.3 \mu\text{m}$. In the BAM images shown here, a blue color scale was chosen to enhance imaging contrast. Light and dark blue areas correspond to regions with high and low lipid coverage, respectively.

3. Results and discussion

3.1. pH effects on DPPA monolayers

The Π - A compression isotherms of DPPA on water at different pHs without added salts are shown in Fig. 1. The region before lift-off as shown in the DPPA isotherm at pH 5.6 corresponds to the gaseous (G)-liquid-condensed (LC) coexistence phase of DPPA. Lift-

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