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# Diffusional motion as a gauge of fluidity and interfacial adhesion. Supported alkylphosphonate monolayers

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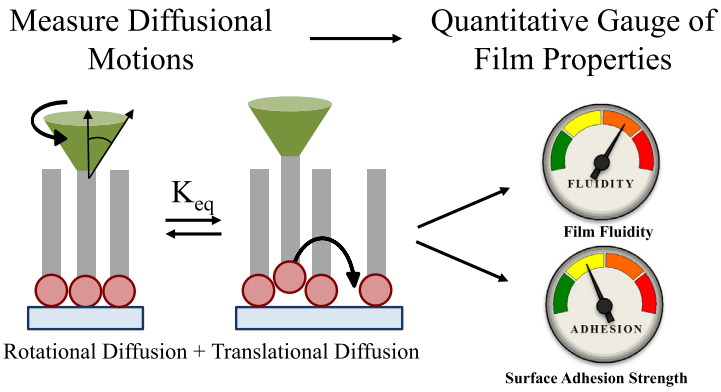
## HIGHLIGHTS

- Quantitation of interfacial molecular motion over a range of length scales.
- Versatile methodology for use of diffusion data to quantitate the strength of supported monolayer adhesion.
- Elucidation of the effects of aggregation on chromophore dynamics and surface adhesion.

## GRAPHICAL ABSTRACT

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## ABSTRACT

We report on the use of diffusion measurements to gauge the fluidity and surface binding properties of a molecular monolayer. The monolayer film consists of octadecyl-1-phosphonic acid (ODPA) and controlled amounts of a lyso-phosphatidic acid tagged with the fluorescent probe BODIPY (BLPA). The monolayer films were formed using a Langmuir–Blodgett (LB) trough and deposited onto a glass slide. Monolayer morphology was characterized during film formation using Brewster angle microscopy (BAM). Fluorescence Recovery After Photobleaching (FRAP) microscopy was used to measure translational diffusion of BLPA and Fluorescence Anisotropy Decay Imaging (FADI) was used to measure rotational diffusion of the BLPA chromophore. These results provide information on the motional freedom of the probe and, importantly, on the strength of interaction between the probe and the support. Compositional variations in the monolayer give rise to changes in constituent dynamics that reflect intermolecular interactions.



## 1. Introduction

Monolayer films have been examined extensively over the past half-century because of their ability to alter the properties of an interface for a desired purpose. A single layer of molecules can be used to change the polarity of a surface, or to mediate electron transfer, for example. With technology requiring ever smaller dimensions, it is important to gain molecular-level control over not only the chemical identity of interfacial layers, but also to be able to control their physical properties [1]. We have undertaken the examination of a representative interfacial monolayer with the aim of quantitating the fluidity and adhesion of the adlayer to the interface. Understanding interfacial dynamics is a prerequisite to controlling these properties.

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One family of monolayer films that has received extensive research attention is self-assembled monolayers (SAMs) of alkanethiols on gold [2–13]. That work has demonstrated the delicate balance of forces required to produce a monolayer and at the same time many practical applications have stemmed from this chemical system, including patterned interfaces for lithographic and other applications [14–17]. In addition to the alkanethiol SAMs, Langmuir–Blodgett (LB) films have enjoyed wide use [18–21]. The interactions between the amphiphilic film constituents and the supporting surface are fundamentally different for the two systems, with physical robustness favoring alkanethiol SAMs [12,13]. LB films, however, allow for greater control over composition and ordering, and also produce films that exhibit controllable mobility [22]. This latter feature is important especially in cases where films benefit from defect mitigation or the ability to adapt to interfacial features. Both approaches to monolayer film formation allow complex molecules to form well-ordered two-dimensional assemblies. For both systems, an understanding of the interrelationship between the nanoscale heterogeneities at the support surface and defects within the film itself, and their effect(s) on the long-range order of the films, remains to be developed fully.

Previous work by the Talham group has shown that films of considerable ordering and structure can be prepared using LB methodology using organophosphonic acids with divalent metals at the appropriate subphase pH [23,24]. We are concerned with the introduction of structural heterogeneities into an amphiphilic monolayer structure, and how the film dynamics and organization change with the amount of "defect" species present. We use octadecylphosphonic acid (ODPA) as the amphiphile for the formation of the LB film and a fluorophore-tagged lysophospholipid (BLPA) as the dissimilar defect molecule. Because BLPA contains the BODIPY chromophore, it also serves as the optical probe in this work. We have chosen to use phosphonate LB films in this work because, ultimately, there is greater structural versatility and range of dynamics available with phosphonates than the corresponding carboxylates [23–29].

We use the BLPA probe to measure the diffusional properties on both short (molecular) and long (μm) length scales using rotational- and translational-diffusion measurements, respectively. Comparison of these two physical quantities affords quantitative information on the role of the defect molecule in mediating organization within the film and on the strength of interaction between the film and the support. While the study of dynamics in LB and related films is not new [22,30–34], our approach to comparing diffusional processes across a range of length scales is both novel and information-rich. We find that the forces binding the adlayer to the interface exceed those expected for simple physisorption, and more closely approximate the strength of hydrogen bond enthalpies in water. The ability to quantitate such interactions opens the door to better understanding how to control the properties of supported monolayer films and, simultaneously, provides direct information on the molecular motion that characterizes these interfaces.

## 2. Materials and methods

### 2.1. Materials

Octadecylphosphonic acid (ODPA) ($C_{18}H_{39}O_3P$, 97% purity), barium chloride dihydrate ($BaCl_2{\cdot}2H_2O$, Reagent Grade), and tetrahydrofuran (THF, 99.9%) were obtained from Sigma Aldrich and used as received. The chromophore used in these studies was 1-(12-[4-(dipyrromethene boron difluoride) butanoyl] amino) dodecanoyl-2-hydroxy-*sn*-glycero-3-phosphate (ammonium salt) (BLPA) (TopFluor Lyso PA, >99%, Avanti Polar Lipids). Water (18 MΩ cm) was obtained from a Milli-Q Plus water purification system and used for all experiments (Fig. 1).

### 2.2. Langmuir monolayer preparation and LB film deposition

The barium ODPA (Ba-ODPA) LB films were prepared by the Langmuir–Blodgett technique [18–20]. We used a large Teflon® Langmuir trough (KSV Nima) equipped with a dipping mechanism and a platinum Wilhelmy plate attached to a balance with an automated feedback system to maintain a constant surface pressure during film transfer. Herein, we use the term 'Langmuir monolayer' to refer to a monolayer at the air–water interface and LB film to refer to the monolayer transferred to the solid support.

The glass substrates were standard microscope slides (1 mm × 25 mm × 75 mm, Globe Scientific) and were placed in a piranha solution ($1H_2O_2$:$3H_2SO_4$, *Caution! Strong oxidizer!*) for 30 min prior to transfer to the LB-trough for dipping. After cleaning, the substrates were rinsed with water and placed in a covered beaker containing water until they were used for deposition. To produce stable monolayers the subphase was a 5 mM $BaCl_2$ aqueous solution. The subphase pH was measured to be 5.4. The temperature of the subphase was maintained at 23° ± 0.1 °C using a circulating water bath (Fisher) attached to the trough. For each dipping experiment 150 μL of a 1 mg/mL ODPA in THF solution was used for monolayer spreading. Solutions containing 5 mol% BLPA (**BLPA-5**) and 10 mol% BLPA (**BLPA-10**) were prepared by mixing appropriate amounts of the ODPA solution and 1 mg/mL BLPA in THF solution and mixing for 30 s by hand. The amount of solution spread on the surface was calculated to give an initial surface pressure $\pi$ below 1 mN/m. During spreading, care was taken to prevent the spreading needle from touching the surface as well as preventing the surface pressure $\pi$ from rising above 0.5 mN/m in order to ensure complete spreading. After spreading, the monolayer was allowed to equilibrate for 30 min to ensure solvent evaporation and monolayer relaxation, before the barriers were moved inward at 5 mm/min (mean molecular area compression of <1 $Å^2$/min) to compress the surface monolayer to the pressure used for dipping (30 mN/m). The compressed monolayer was allowed to equilibrate for 15 min before it was transferred onto the glass slide. The monolayer was transferred (upstroke) at a dipping speed of 5 mm/min while keeping the pressure constant, covering a total area of 35 mm × 25 mm on each side of the glass slide. The coated slides were dried in air for at least 1 h. before FRAP and FADI measurements were made.

### 2.3. Brewster angle microscopy

We characterize the morphology of the monolayers formed on the LB-trough using a Brewster angle microscope (BAM, Accurion UltraBAM). This instrument is characterized by 2 μm spatial resolution and an adjustable angle of incidence. The laser wavelength used for BAM measurements is 653 nm (diode laser) and the instrument is operated using software supplied by the manufacturer.

### 2.4. Steady state fluorescence measurements

Excitation and emission spectra of the BLPA chromophore in THF was collected using a Jobin Yvon Spex Fluorolog-3 spectrometer. Emission spectra were collected for BLPA in THF as well as the 5 mol% and 10 mol% samples to verify the presence and band positions of the incorporated BLPA chromophore. Spectral resolution was set to 1 nm for both the excitation and emission monochromators for all measurements.