Carbon accumulation at model biological interfaces: Changes to lipid film structure and organization

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Abstract

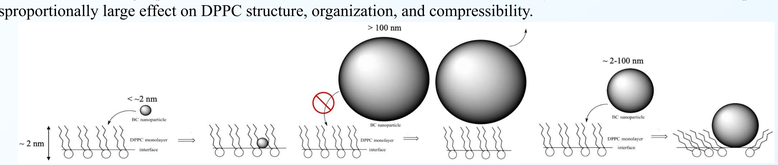
The effects of fine particulate matter (< 2.5 m in diameter, $PM_{2.5}$), particularly black carbon (BC) aerosols, on biological membrane structure, organization and function remain poorly characterized despite the risks these particles pose to human health and the environment. In order to develop a predictive understanding of how non-biological, nano-sized materials impact membrane organization and function, findings presented in this work use model systems to examine how different sized carbon nanoparticles (CNPs) affect the properties of lipid films adsorbed to aqueous – air interfaces as well as lipid bilayers in vesicles. Data from surface tension measurements show that carbon loadings up to 5% in lipid monolayers increase the isothermal compressibility, with higher loadings and smaller sizes of CNPs appearing more like pure DPPC while lower loadings and larger sizes of CNPs have a more extreme effect on monolayer compressibility. Differential scanning calorimetry (DSC) measurements indicate that CNPs in aqueous solution *do not* significantly change DPPC bilayer melting temperature, although the gel-liquid crystalline transition temperature does broaden slightly with low CNP loadings and larger CNP size. These results are supported with complementary surface specific vibrational sum frequency generation (VSFG) experiments. Together, findings presented in this work illustrate how a combination of independent measurement techniques can begin to identify a subtle but measurable particulate affinity for lipid membranes and how these associations depend sensitively on a lipid film's thermodynamic state.

Introduction

BC is a general term that describes a mixture of products resulting from incomplete combustion and this material presents physiological and environmental threats due to its extreme heterogeneity. In the U.S., approximately 35% of BC emissions come from wildfires, 52% from transportation, and the remaining 13% come from the energy and industry sectors. BC aerosols are too small to readily settle out of the atmosphere, and smaller particles can remain suspended in the air indefinitely. BC aerosols in ambient air can collide with other airborne particles to form larger, and even more heterogeneous particles with elemental carbon content up to 50%. Adsorption of BC aerosols to biologically relevant aqueous – air interfaces such as alveoli surfaces causes health risks and is linked to increased mortality rates throughout the world. Specific to pulmonary diseases, BC aerosols change the structural, elastic, and dynamic properties of lung surfactant. Data presented in this poster provide specific, molecularly resolved data that is both quantitative and enables us to be predictive about how non-biological nano-sized materials impact membrane integrity.

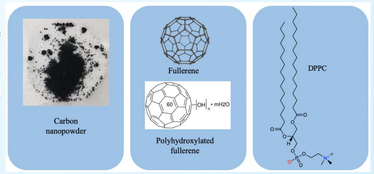
Size effects

Different sized elemental CNPs will irreversibly affect DPPC monolayer structure and organization by packing synergistically with lipid films and introducing new domain structures that change monolayer structure, organization, and dynamic properties.
Smaller particles (< 2 nm) and larger particles (> 100 nm) will have less effect on DPPC monolayers, while intermediate sized particles (2-100 nm) will have a disproportionally large effect on DPPC structure, organization, and compressibility.



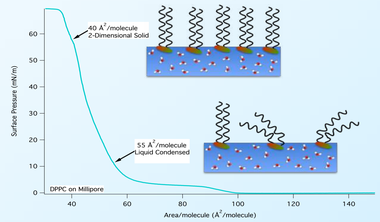
Model systems

To model aqueous interface interactions, representative systems of carbonaceous nanoparticle and insoluble monolayers are used.
Insoluble monolayers were composed of the lipid 1,2-dipalmitoyl-sn-glycerol-3-phosphocholine (DPPC). DPPC is the primary component of lung surfactant and has well characterized surface behavior.

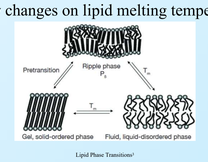


Methods

DPPC undergoes 2-dimensional phase transitions (right). At 40 Å^2/molecule, the DPPC is in the 2-dimensional solid phase and is tightly packed. At 55 Å^2/molecule, the DPPC is in the liquid condensed phase, and is a more loosely packed monolayer. The Langmuir trough surface tension results shown here correspond to the 55 Å^2/molecule phase.

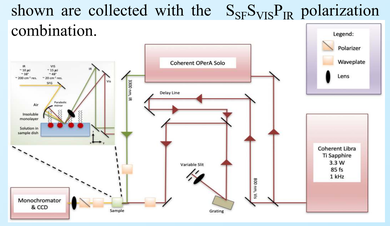


Differential scanning calorimetry (DSC) experiments can be relevant to observing interactions in biological systems by providing information about whether CNPs are able to migrate through a membrane (i.e. lungs) and integrate themselves in into the membrane. DSC is also used to study changes on lipid melting temperatures.

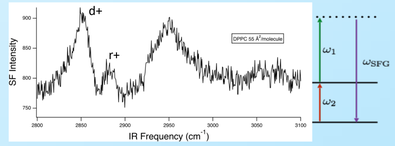


Lipid Phase Transitions[5]

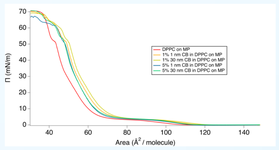
Vibrational sum frequency generation (VSFG) is a coherent nonlinear technique. Two pulsed electromagnetic fields matched in time and space create a third field with a frequency equal to the sum of the frequencies of the incident fields. Incident pulses are at a visible (800 nm) and IR frequency (3,300 nm). By tuning the IR frequency to a vibrational mode, the surface specific vibrational spectra is measured. Spectra shown are collected with the $S_{SF}S_{VIS}P_{IR}$ polarization combination.



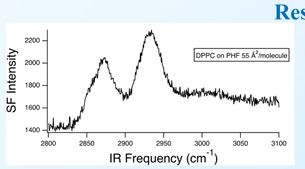
In the DPPC SFG spectrum below, r+ corresponds to methyl symmetric stretching and d+ corresponds to methylene symmetric stretching, where r+/d+ will give relative orientation.

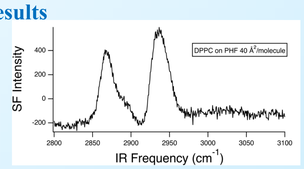


Results

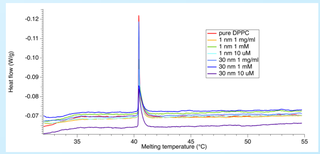


- Langmuir trough experiments measure changes in monolayer surface pressure (and free energy) with respect to area
- The results shown here correspond to the 55 Å^2/molecule phase
- Including fullerene (~1 nm) and carbon nanopowder (~30 nm) in DPPC monolayers causes a decrease in collapse pressure and a decrease in lipid film compressibility





- VSFG is a surface specific technique that probes vibrational signatures of molecules at a surface
- Here are SFG spectra in the CH stretch region with SSP polarization (vibrations with IR transition moment normal to the surface) at 55 Å^2/molecule (left) and at 40 Å^2/molecule (right) of DPPC on water soluble polyhydroxylated fullerenes (PHFs) in Millipore
- The interactions between PHFs in the bulk and the DPPC at the surface lead to peak broadening and an increase in r+ intensity in comparison to DPPC on Millipore water
  - The PHFs in the bulk have a condensing affect on the lipid monolayer



- DSC measures a membrane's gel-liquid crystalline transition temperature
- DPPC vesicles continued to show a melting temperature of 41˚ for all CNP concentrations tested
  - CNPs did not intercalate into the membranes
- Melting temperatures *did* broaden suggesting some interaction mechanism between CNPs and the lipid head groups

Conclusions

- Lipid films exhibit decreased film rigidity with the addition of different sized CNPs
- Small concentrations of carbon nanopowder (30 nm) decreases film rigidity more than small concentrations of fullerene (~1 nm) does
- PHFs (in bulk) have some sort of affinity for DPPC, with their interactions leading to increased film rigidity
  - What is the mechanism (i.e. cooperative adsorption)?
- The melting temperature of DPPC does not change with incorporation of different sized and varying concentrations of CNPs
- Peak broadening in DSC measurements does suggest that CNPs interact with DPPC

References

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