phosphate backbone and their impact on the folding free energy, we have formulated a mathematical treatment for computing the volume of the main-chain torsion using end group pressure-volume-temperature data for phospholipid vesicles. We compare the computed conformational entropies against a statistical free energy analysis of structures in the crystallographic database from several thousand phospholipid and oxysterol assemblies. The oxysterols 20, 22, 25, and 27 hydroxycholesterol were selected and compared with the 25-hydroxycholesterol/DPPC system. Specifically, an upper and lower miscibility phase transition were observed in these systems. In all of these systems phase transitions were consistent with the 25-hydroxycholesterol/DPPC system. The oxysterol concentration has been correlated with cell death. The oxysterol was confirmed. We present a model for oxysterol behavior within lipid monolayers based on the presence and location of the two hydroxyl groups on the oxysterols. Consistent with our model we find the lower transition pressure increases with increasing distance between the two hydroxyl moieties. Pressure-area isotherms, fluorescence microscopy, analysis of domain size distribution, phase fraction measurements, isobaric cuts, and phase diagrams will be used to support our model of phospholipid/oxysterol interactions.

Membrane Physical Chemistry I

1459-Pos Board B189
Effects of Oxidized Lipid Species on Permeability of Giant Unilamellar Vesicle Membranes
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Oxidation of unsaturated lipids in cellular membranes has been shown to cause severe membrane damage and potentially cell death. Even in low concentrations, oxidized lipid species are known to cause changes in the membrane structure, such as decreased fluidity. Vesicles containing concentrations of oxidized species as low as 20mol% total lipid concentration can display the spontaneous formation of pores. Below this poration limit, the effects of oxidation on membrane permeability have not been quantified. Here, we use giant unilamellar vesicles (GUVs) as a system to measure passive transport across membranes containing defined concentrations of oxidized lipid species. GUVs consisting of a saturated phospholipid, an unsaturated phospholipid, and cholesterol were used as a model membranes. By replacing defined amounts of the unsaturated lipid with a corresponding oxidized product, the oxidation process could be mimicked, yielding vesicles of varying oxidized lipid concentration. Oxidized lipid concentration was varied from 0mol% to 15mol% of the total lipid concentration. We measured passive transport across the membrane using a microfluidic trap to capture the vesicles and spinning disk confocal microscopy to track the transport of a fluorescently labeled short-chain poly(ethylene glycol) species of various molecular weights to track the diffusion of a representative small molecule. Membrane permeability was determined by fitting the resulting concentration profiles to a finite element model of diffusion and permeation around and through the membrane. Experiments showed that an increase in oxidized concentration increases membrane permeability. As passive transport is an important mechanism for drug delivery, understanding the relationship between oxidation and permeation could provide insight into the pharmaceutical characteristics of oxidized cells.

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The Influence of Hydroxyl Position on Oxyesterol/Phospholipid Monolayer Phase Behavior: Experimental Results and Model
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Oxysterols are naturally produced by enzymatic and non-enzymatic processes. Increased oxysterol concentration has been associated with cell age, membrane thinning in model systems, and several pathologies. It has been previously reported that mixed phospholipid monolayers containing 25-hydroxycholesterol exhibit anomalous phase behavior compared to similar cholesterol containing monolayers. We present a systematic series of Langmuir monolayer and fluorescence microscopy studies which focus on the role of the positions of the hydroxyl moieties in different oxysterols. The oxysterols 20, 22, 25, and 27 hydroxycholesterol were selected and mixed with DMPC for compositions from 10 - 90 mole percent oxyesterol (increments of 10 percent were chosen). In all of these systems phase behavior was consistent with the 25-hydroxycholesterol/DPPC system. Specifically, an upper and lower miscibility phase transition were observed in all systems for oxysterol concentrations less than 40 mole percent and a discontinuity in the pressure-area isotherm directly tracked the lower miscibility transition pressure. Likewise the area-expansion due to the presence of the oxysterols was confirmed. We present a model for oxyesterol behavior within lipid monolayers based on the presence and location of the two hydroxyl groups on the oxysterols. Consistent with our model we find the lower transition pressure increases with increasing distance between the two hydroxyl moieties. Pressure-area isotherms, fluorescence microscopy, analysis of domain size distribution, phase fraction measurements, isobaric cuts, and phase diagrams will be used to support our model of phospholipid/oxysterol interactions.