Phospholipid monolayer/water interfaces

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Phospholipid Molecular Structures

Chain Lengths
- DM : Dimyristoyl (C₁₄)
- DP : Dipalmitoyl (C₁₆)
- DS : Distearoyl (C₁₈)

Phosphatidylcholine (PC)
Phosphatidylethanolamine (PE)
Phosphatidylglycerol (PG)
Phosphatidylserine (PS)
Vibrational Sum-Frequency Studies of a Series of Phospholipid Monolayers and the Associated Water Structure at the Vapor/Water Interface

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The orientation and conformation of phospholipid monolayers and the structure of water associated with these monolayers adsorbed at the vapor/water interface have been investigated using vibrational sum-frequency spectroscopy. The phospholipids studied are saturated diacyl phosphatidylcholines, phosphatidylethanolamines, phosphatidylglycerols, and phosphatidylserines with chain lengths of 14, 16, and 18 carbons. Spectra have been acquired under different polarization schemes for monolayers at the vapor/D$_2$O interface to examine chain ordering and at the vapor/H$_2$O interface to examine water structure. Comparisons are made between the monolayers based on chain length and headgroup differences. These studies show significant differences between the aqueous environments associated with the zwitterionic lipids and the charged lipids.
SSP SFG
C–H stretching region

Assignments
- $\text{CH}_2\text{SS} : \sim 2850 \text{ cm}^{-1}$
- $\text{CH}_3\text{SS} : \sim 2880 \text{ cm}^{-1}$
- $\text{CH}_2\text{FR} : \sim 2897 \text{ cm}^{-1}$
- $\text{CH}_3\text{FR}^* : \sim 2940 \text{ cm}^{-1}$

*the possibility of some contribution from $\text{CH}_2\text{AS}$

relative disorder for $\text{C}_{14}$ chains and
relatively strong order for $\text{C}_{18}$ chains

DM (C$_{14}$), DP (C$_{16}$), DS (C$_{18}$)
Assignments

CH$_{3AS}$ : 2960 cm$^{-1}$
CH$_{2AS}$ : btw 2897 and 2910 cm$^{-1}$

The intensity of the CH$_3$ as a function of chain length
- the longer chain length the higher intensity of the CH$_3$ and the methyl groups are oriented strongly
- low intensity of the CH$_3$ means the methyl groups are oriented isotropically about the surface normal
Water Structure

Enhanced intensity due to increased alignment of water molecules

at the vapor/H$_2$O interface at pH 7.0 (10 mM phosphate buffer)
pH effect

- ssp

DMPS

- no affect for PC, PG, PS (not shown)

DMPE

- salt does have a large effect on the intensity
• C14 < C16 < C18 : chain ordering of the phospholipid.

• Phospholipid monolayers increase the orientation and bonding of water molecules.

• Excess salt for the charged lipids (PG and PS) has a large effect on the orientation of water molecules.

• It has a negligible effect on the orientation and hydrogen bonding of water molecules associated with the monolayers of the zwitterionic lipids (PC and PE).
Interfacial Water Structure Associated with Phospholipid Membranes Studied by Phase-Sensitive Vibrational Sum Frequency Generation Spectroscopy

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Abstract: Phase-sensitive vibrational sum frequency generation is employed to investigate the water structure at phospholipid/water interfaces. Interfacial water molecules are oriented preferentially by the electrostatic potential imposed by the phospholipids and have, on average, their dipole pointing toward the phospholipid tails for all phospholipids studied, dipalmitoyl phosphocholine (DPPC), dipalmitoyl phosphoethanolamine (DPPE), dipalmitoyl phosphate (DPPA), dipalmitoyl phosphoglycerol (DPPG), and dipalmitoyl phospho-L-serine (DPPS). Zwitterionic DPPC and DPPE reveal weaker water orienting capability relative to net negative DPPA, DPPG, and DPPS. Binding of calcium cations to the lipid phosphate group reduces ordering of the water molecules.
water on pH = 13

VSFG spectra
Negatively charged: DPPA, DPPG, DPPS

All negatively charged phospholipids order the water molecules with hydrogens pointing up.
DPPC, DPPE, DPPC on 0.4 CaCl$_2$

Ca$^{2+}$ ions would favor binding to the phosphate.

The water molecules with hydrogens pointing up.

DPPC, DPPE, DPPC on 0.4 CaCl$_2$
water orientation becomes less ordered at the interface in the presence of Ca$^{2+}$ ions

blue shifts: calcium binding results in phosphate dehydration

DPPC phosphate group
Conclusion

• Negatively charged head groups PA, PG and PS have greater impact on water ordering than neutral zwitterionic head groups PC and PE (same as Richmond’s group).

• The negative charge of zwitterionic phospholipids on the phosphate group dominates the interfacial water orientation.

• Binding cations to the lipid phosphate group reduces ordering of the water molecules.