

Disentangling Infrared CH Bands Arising from Polar and Apolar Domains of Phospholipids: Headgroup CH Moieties are Involved in Water Binding

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The polar region of lipid molecules is equipped with sites suitable for electrostatic and hydrogen-bonding interactions that are important for both their propensity to assemble to higher-order structures, usually bilayers, and the binding or embedding of other functional unities, as membrane proteins. Knowing the interaction potency of lipid headgroups is, thus, a prerequisite to understand the pathways related to biomembrane functions.

An ideal probe molecule to explore the binding behavior of lipid aggregates (as of any molecule with polar regions) is water as it combines manifold H bonding potentialities with a small size largely excluding steric problems. We have applied infrared spectroscopy to study the hydration of phosphatidylcholines (PCs) according to a protocol developed in this laboratory [1] in terms of the specific contributions of the different lipid components for water binding. Beside the well known binding centers, as phosphate and carbonyl groups, CH (i.e. methyl, methylene and methine) groups, which are not easily accessible by experimental means, are present in the polar lipid region. To visualize the pertinent CH vibrational bands, which are practically hidden in the spectra of common lipids because of complete overlap by the predominant chain CH bands, a chain-depleted model compound, methyl-PC [2], as well as different specifically deuterated dimyristoyl-PCs as “complete” lipid molecules have been used. Systematic variation of the isotopic-exchange pattern made it possible to disentangle the CH stretches by separating from each other the different molecular regions of a phospholipid, that is headgroup, glycerol backbone and hydrocarbon chains [3]. CH (or CD) stretching vibration bands due to methyl and methylene groups located in methyl-PC or in the polar region of dimyristoyl-PCs surprisingly undergo dramatic hydration-driven wavenumber upshifts by as much as 6-20 cm⁻¹. As these shifts are relatively strong referred to the 2 cm⁻¹ wavenumber increase commonly found for the lipid chain-melting process, which in fact represents a conformationally demanding (i.e. the main) transition, they can be considered as indicating a direct water binding to the CH groups in the polar lipid domain rather than merely conformational changes.

This suggestion is supported and rationalized by theoretical calculations performed for methyl-PC that reveal, among other structural and molecular-physical phenomena, instances of (lipid-)C-H...OH₂ hydrogen bonding to explain the spectroscopic findings [4]. The formation of these weak C-H...O H bonds might be promoted by the presence of the electrophilic substituents located next to the CH groups in the polar lipid domain.

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