STUDIES OF WATER DIFFUSION IN THE VICINITY OF SINGLE-SUPPORTED LIPID MEMBRANES

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ABSTRACT

Previous quasielastic neutron scattering measurements on lipid membranes have used samples of large stacks of membranes with an unknown amount of water between layers. This geometry complicates interpretation and renders comparison to molecular dynamics simulations difficult. Instead, this work investigates water dynamics on single supported bilayers of the model charge-neutral lipid DMPC (dimyristoyl-sn-glycero-3-phosphocholine) and its anionic analogue DMPG (dimyristoyl-sn-glycero-3-phosphoglycerol). Single bilayers can be more directly compared to molecular dynamics simulations, can be interrogated with Atomic Force Microscopy, and avoid the uncertainty in quantifying the amount of water in samples.

A novel method for producing the anionic bilayers is developed, which is a variant of the vesicle fusion method. Atomic Force Microscopy is used to characterize the quality of both DMPC and DMPG membranes supported on SiO$_2$-coated silicon substrates. Measuring the bilayer thickness as a function of temperature reveals that the gel-to-fluid phase transition is found to be significantly shifted to higher temperatures for adsorbed lipid bilayers in air compared to free vesicles in solution.

The temperature-dependent quasielastic spectra from hydrated DMPC bilayers reveal three types of membrane-associated water. First, a large amount of water diffuses similarly to bulk supercooled water and freezes at 265 K. Second, a smaller amount of water closer to the membrane diffuses more slowly than bulk supercooled water at the same temperature and freezes continuously from 265 to 250 K. Third, 8–11 water molecules per lipid diffuse on the same nanosecond timescale as H atoms within the lipid molecules, suggesting that they are bound to the lipid headgroups, and remain mobile to 250 K.

Water near the anionic membrane behaves qualitatively different than near the neutral lipid. For the DMPG membrane, no evidence of a bulk-like freezing transition is seen; instead, water freezes continuously down to 200 K. We speculate that this behavior may be caused by a film-like water morphology, owing to the relative hydrophilicity of the DMPG lipid surface, whereas the hydrophobic DMPC surface supports the dewetting of ice and the formation of bulk-like hexagonal ice. Evidence for this hypothesis include the complete melting of water near the DMPG membrane below the bulk point for samples regardless of total hydration.