

Electrostatic interactions in phospholipid membranes: influence of ions and hydroxyl radicals

Christiane A. Helm

Institute of physics, University of Greifswald, Felix-Hausdorff-Straße 6,
17489 Greifswald, Deutschland.

Electrostatic interactions in monolayers of acidic phospholipids are studied by thermodynamical and optical techniques in conjunction with model calculations. The focus is the LE/LC (liquid expanded/liquid condensed) phase transition. The phase transition pressure depends on the composition of the aqueous solution. For cardiolipins and monovalent cations (Na^+ , K^+ , Cs^+) weak binding and a nonmonotonic behavior of the phase transition surface pressure is found: Raising the monovalent salt concentration increases the transition surface pressure by charging the TMCL monolayer until 0.1 mol/l, then screening effects dominate and decrease the transition surface pressure by reducing electrostatic repulsion between lipid head groups. Strong binding for divalent cations is found, in the sequence $\text{Sr}^{2+} < \text{Mg}^{2+} < \text{Ca}^{2+} \approx \text{Zn}^{2+} \approx \text{Mn}^{2+}$.

The reaction of DPPC monolayers with hydroxyl radicals (HO^\cdot from Fenton solutions) was investigated using infrared reflection absorption spectroscopy (IRRAS), grazing incidence X-ray diffraction, X-ray reflection and fluorescence microscopy. The DPPC monolayer is exposed to different HO^\cdot concentrations. The decrease in the lateral pressure was used as a measure of the efficiency of the HO^\cdot attack. With increasing HO^\cdot concentration, the surface transition pressure decreased; eventually it disappeared. Fluorescence microscopy during the HO^\cdot attack showed that new domains in the condensed phase nucleate immediately. In the LC phase a reduced tilt angle of the alkyl chains was found. IRRAS experiments indicated a partial cleavage of the head group leading to a reduced head group size, the reduced phase transition pressure is attributed to Fe^{2+} binding.