

Cation-induced changes to the structure of lipid membranes

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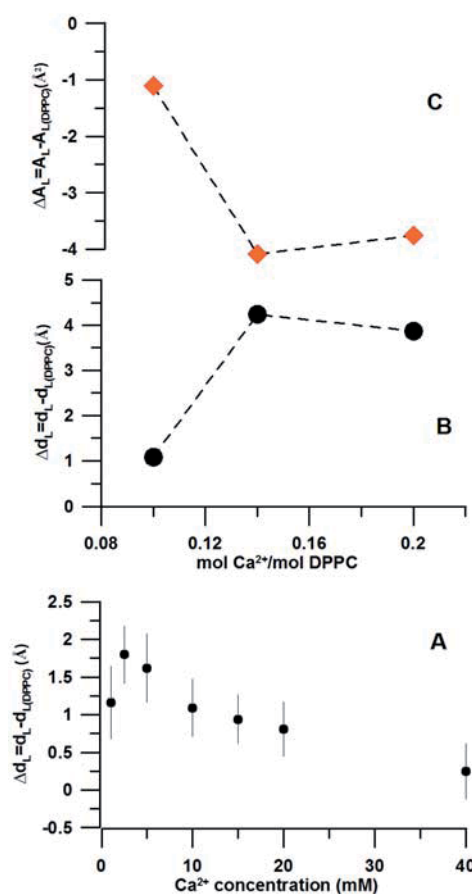
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Cell membrane properties such as, membrane fluidity, bending and rigidity moduli, electrostatics, and aggregation and fusion are tightly associated with ions that are prevalent in both the cytosol and the exterior of the membrane. The cation binding (Ca^{2+} , Mg^{2+} , etc) depends not only on the property of the cation and the membrane lipid head-group, but also on the lipid tail chain. In spite of many studies of cations adsorption on phosphatidylcholine membranes, the information concerning their influence on the lipid bilayer itself is rather scattered and often contradictory. Former hydration X-ray diffraction experiments reported no effect of Ca^{2+} on the dipalmitoylphosphatidylcholine (DPPC) bilayer thickness in a lamellar phase [1], while NMR experiments documented an increase in order parameters in the polar head group segments as well as hydrocarbon chains [2], and changes in the surface area per phospholipid molecule [3]. The molecular dynamics simulation results revealed condensation of an anionic lipid bilayer and a concomitant increase in lipid order parameters [4]. Interestingly, in contrast to K^+ and Na^+ , Ca^{2+} , was found to play a dominant role in affecting bilayer structure. Recent small-angle neutron-scattering (SANS) measurements using DPPC vesicles and Ca^{2+} have revealed that cations at low concentration increase the order of lipid bilayers by increasing bilayer thickness (Fig. 1A) and decreasing area per lipid [5,6].

We have studied the interactions of calcium with the biomimetic membrane, DPPC. The performed small-angle neutron-diffraction (SAND) experiment on oriented multilamellar samples complements the initial SANS measurements [5,6]. The experiment was proposed with the aim to decouple effects due to electrostatics interactions from those of geometrical constraints found in curved vesicular bilayers [7].

DPPC oriented multilayers at three molar ratios Ca^{2+} :DPPC were prepared by hydrating thin lipid films from vapors at defined humidity. Samples were hydrated with different $\text{D}_2\text{O}/\text{H}_2\text{O}$ solutions (100%, 70%, 40%, and 8% D_2O) to vary the scattering contrast between the multilayers of lipid bilayers and water. The difference of such data directly results in the water distribution profiles. In addition, contrast variation approach allows one to solve the phase problem necessary for the Fourier reconstruction of the one-dimensional scattering length density profiles [8].

Fig. 1 A) The effect of Ca^{2+} on the curved DPPC lipid bilayer thickness obtained by SANS. The SAND results of change in the planar DPPC lipid bilayer thickness Δd_L (B), and the surface area per DPPC molecule ΔA_L (C) induced by Ca^{2+} binding.



Attained results (summarized in Fig. 1B,C) show clearly that Ca^{2+} effects DPPC bilayer thickness (d_L). Due to Ca^{2+} binding, we found its increase up to $\Delta d_L = d_L - d_{L(\text{DPPC})} = 4.2 \text{ \AA}$, where $d_{L(\text{DPPC})}$ is the lipid bilayer thickness without any Ca^{2+} . A concomitant decrease in surface area A_L per DPPC molecule was also determined. Our observations agree well with previous SANS results [5,6] confirming the Ca^{2+} induced structural changes to bilayer based on a prevailing effect of electrostatic interactions, rather than that of bilayer curvature.

Acknowledgments

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References

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