Abstracts

– 16. Membranes and Vesicles –

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Membrane activity of pentaene macrolide didehydroroflamycoin investigated in model lipid bilayers

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Didehydroroflamycoin (DDHR) was shown to have antibacterial and antifungal activity. However, its mechanism of action has not been investigated so far. Antibiotics from this family have membrane activity, their biological action is localized in the membrane, and the membrane composition and physical properties facilitate the recognition of a particular compound by the target organism. We use GUVs for a study of the action of DDHR. Results from experiments are compared with the action of filipin III and amphotericin B, and the behavior observed for DDHR is described in the context of that of these compounds. The study shows that DDHR disrupts membranes via two different mechanisms and that the involvement of these mechanisms depends on the presence of cholesterol. The leakage assays performed in GUVs and the conductance measurements using BLM reveal that the pores developed in the absence of cholesterol are transient and their size depends on the DDHR concentration. In contrast, cholesterol promotes the formation of more defined structures that are temporally stable.
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Cation-induced changes to the structure of lipid membranes

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Cell membrane properties such as membrane fluidity, bending and rigidity moduli, electrostatics, and aggregation and fusion are associated with ions that are prevalent in intra/extra-cellular environment. The cation binding depends strongly on the property of the cation and the membrane lipid head-group. We have studied the interactions of calcium and zinc with the biomimetic membrane made of DPPC. The small angle neutron diffraction from oriented multilamellar samples was utilized. Attained results show clearly differences in the effects of the two cations. For both, a bilayer thickness increases due to divalent metal ion (Me^{2+}) binding, reaching the maximum at stoichiometry Me^{2+}:DPPC$\sim$1:7 mol/mol. However, while the further increase in Ca^{2+} results in a bilayer thinning down to the level of pure DPPC, the Zn^{2+} binding saturates. Our observations can most likely be rationalized in terms of electrostatic interactions, and thus reinforces the special importance of these cations. Zinc possesses a higher affinity to electronegative moieties such as ester and/or carbonyl groups involving them in the complex formation. MD simulations have been performed to gain more detailed information.
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Monte Carlo simulation studies toward divalent ions membrane fusion initiation

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Molecular processes leading to ion-induced fusion of the lipid membrane still remain unexplored. It has already been shown that changes in the organization of the polar part of the lipid membranes, forced by electric field, involve changes in the packing of the hydrocarbon chains of lipid molecules. Based on these results, the effect of divalent ions on the stability of the lipid membrane, is examined. Changes of energy of the system and the average membrane area per lipid chain in response to a fixed position of a divalent ion are studied using Monte Carlo simulation technique. The distance between the ion and the border of hydrophobic and hydrophilic membrane part varied from 5 to 0.5nm. The membrane in gel phase responds with decrease in chain packing for the ion distance in range from 3 to 1.5nm. For closer distances, the membrane bifurcation has been observed: depending on the initial state the membrane increases or decreases its area. The membrane in the liquid crystalline phase begins to respond to ion distance from 25 to 10nm by increasing its surface. For closer distances the membrane response has been similar to the membrane in gel phase. Based on the results, the model of molecular changes, initiating the process of membrane fusion induced by ions, has been proposed.

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Self-assembly of membranes at solid-state nanopores for membrane sensing

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Solid-state nanopores enable investigations of membrane functionalities on close to the molecular length scale; they can be used for both patch-clamp-type probing of transport across membranes and integration with nanoscale sensing schemes such as nanoplamonic readout of molecular interactions and structural changes. We present a platform for creation of nanopore arrays using colloidal lithography, compatible with a range of sensor approaches including optically resolving individual nanopores. The fabrication process is integrated with an approach to molecular functionalization of the nanopores to control membrane assembly around and at the pores. We demonstrate that without selective nanopore functionalization supported membranes self-assembled from liposomes will only span a fraction of pores[(1)]. However, selective pore functionalization allows us to position vesicles and fuse membrane material exclusively over the pore. The nanopore structure is used to fabricate a nanoplasmonic sensor able to simultaneously selectively detect liposome binding events at the top of the nanopore structure and at its bottom[(2)].
(1) Kumar, K.; Isa, L. et al. Langmuir ***2011****, 27, 10920.*
(2) Kumar, K.; Dahlin, A. B., et al. Nano Lett. ***2013****, 13, 6122.*