Ions Interacting with Membranes and Polymers and in-between Comes Water

Rumiana Dimova 06.04.1971
1995: Diploma, Chemistry (Sofia University, Bulgaria), Major: Chemical Physics and Theoretical Chemistry, Thesis: Role of the Ionic-Correlation and the Hydration Surface Forces in the Stability of Thin Liquid Films
1997: Second MSc (Sofia University, Bulgaria) Thesis: Interactions between Model Membranes and Micron-Sized Particles
1999: PhD, Physical Chemistry (Bordeaux University, France) Thesis: Hydrodynamical Properties of Model Membranes Studied by Means of Optical Trapping Manipulation of Micron-Sized Particles
2000: Postdoc (Max Planck Institute of Colloids and Interfaces, Potsdam)
Since 2001: Group Leader (Max Planck Institute of Colloids and Interfaces, Potsdam)

Ion-membrane interactions are important for the physiological activity of cells as they are inherent to almost every cellular process. Synthetic polymers on the other hand are artificial analogs to macromolecules like proteins and nucleic acids whose conformation and properties also strongly depend on the presence of ions. One example of ion-protein interactions is the renowned but still poorly understood Hofmeister series, which arranges different ions according to their ability to induce precipitation of egg white proteins. Overall, the behavior of both, membranes and polymers (artificial or natural), is influenced by interactions with ions. Intuitively, one would expect that electrostatic forces have the most prominent contribution to these interactions. However, the experiments we have performed in the last few years show that the polar character of a trivial molecule like water plays an even more important role. We have found that changes in water structure, i.e., destroying and reforming hydration shells, breaking hydrogen bonds, appears to be the driving force in many ion-membrane and ion-polymer interactions.

A convenient technique for studying these processes is isothermal titration calorimetry (ITC). ITC can be used to measure ion-membrane and ion-polymer interaction enthalpy. When an appropriate model is applied, the titration calorimetry data can be used to extract the equilibrium constant of the process, i.e., characterize the stoichiometry of the interaction. Calcium, chromium and lanthanide ions (like europium and gadolinium) are among the ions that have been studied in our lab **[1-3]**. They were used to probe the properties and stability of large unilamellar vesicles (~100nm in size). All of the ions yield endothermic signals when titrated into the vesicle solution. Even when the lipid membrane is negatively charged, calcium was found to interact with an endothermic signal ($\Delta H>0$) **[1]**.

The results obtained were consistent with measurements investigating ion-polymer interactions. We studied adsorption of calcium to polymers having the same functional groups as those of the charged membranes **[4]**. Once again, the driving factor of the process was found to be the entropy gain from liberating water molecules (see **Fig. 1B**).

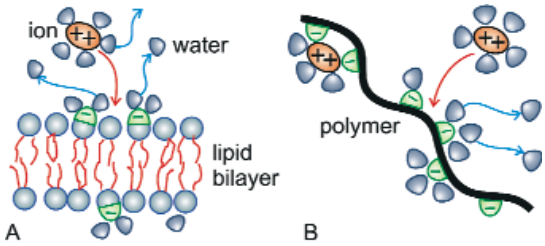

Fig. 1: Schematic presentation of the interaction of a multivalent cation with a negatively charged lipid bilayer (A) and with a polymer (B). The ion size is exaggerated for clarity. The process is driven by the liberation of water molecules from the hydration shells of the ions and the membrane/polymer charges.

The interaction of calcium with polymers was also studied in the context of crystal growth and scale inhibition. In a similar fashion, binding of polymers to calcite crystals was found to be endothermic and entropy driven **[5]**. This indicates that structure of water plays an important, currently not fully recognized role in the control of mineralization processes.

We have found that the ion-membrane and ion-polymer interaction is endothermic ($\Delta H>0$). For the measured processes to occur spontaneously, the condition $T\Delta S>0$ (where T is temperature and ΔS is entropy change) has to apply which implies that the interactions are entropically driven. The gain in entropy is presumably due to destruction and reassembly of hydrations shells finally resulting in the liberation of water molecules, see **Fig. 1**. All of our results point to the importance of the restructuring of water as a driving force in ion-membrane and ion-polymer interactions.

In addition to the thermodynamic characterization we are able to observe the ion-membrane interaction directly using microscopy. Our measurements on giant unilamellar vesicles (~10μm in radius) show that multivalent ions induce adhesion between two neutral membranes **[2, 3]**. In addition, small amount of europium or calcium ions were found to cause membrane rupture presumably due to ion-generated membrane tension. The current working hypothesis is that the ions have condensing effect on lipid molecules, i.e. they reduce the area per lipid, thus bringing about membrane tension and causing eventual rupture.

R. Dimova, M. Antonietti, T. Franke, C. Haluska, R. Lipowsky, Y. Mastai, C. Sinn
Rumiana.Dimova@mpikg.mpg.de

References:

[1] Sinn, C., Antonietti, M. and Dimova, R.: Binding of calcium to phosphotidylphosphoserine membranes. in preparation.
[2] Franke, T.: Haftübergang von Lipid-Vesikeln: Effekt von $CrCl_3$ auf PC-Membranen. PhD Thesis (2003).
[3] Haluska, C.: Interactions of functionalized vesicles in the presence of europium (III) chloride. PhD Thesis (2005).
[4] Sinn, C., Dimova, R. and Antonietti, M.: Isothermal titration calorimetry of the polyelectrolyte/water interaction and binding of Ca^{2+}: Effects determining the quality of polymeric scale inhibitors. Macromolecules, **37**, 3444-3450 (2004).
[5] Dimova, R., Lipowsky, R., Mastai Y. and Antonietti, M.: Binding of polymers to calcite crystals in water: Characterization by isothermal titration calorimetry. Langmuir **19**, 6097-6103 (2003).