

A CALORIMETRIC STUDY OF PHOSPHOLIPID HYDRATION

Natalia Markova¹, Emma Sparr¹, Lars Wadsö² and Håkan Wennerström¹

¹Physical Chemistry 1, Center for Chemistry and Chemical Engineering, University of Lund, P.O. Box 124, S-221 00 Lund, Sweden

²Division of Building Materials, University of Lund, Box 118, S-221 00 Lund, Sweden

Abstract

We present a novel method for monitoring isothermal lipid hydration using a sorption microcalorimeter [1]. A measuring cell of the double twin calorimeter [2] consists of two vessels connected by a stainless steel tube. The upper vessel contains pure water and the bottom vessel is loaded with the lipid sample. This calorimeter allows for simultaneous measurement of the partial molar enthalpy and the chemical potential (or the partial molar free energy) of the water. The versatility of the method is demonstrated by studies of the hydration of the phospholipids dipalmitoyl phosphatidylcholine (DPPC), dimyristoyl phosphatidylcholine (DMPC) and dilauroyl phosphatidylecholine (DLPC) at 25 and 27°C. The measurements provide a relation between water content and water chemical potential, which in these lamellar systems is often recast as a force-distance relation and has been called the hydration force. Through the simultaneously monitored calorimetric values the partial molar enthalpy of water is also obtained. The method consequently provides a rather unique combination of information on both partial molar enthalpy and partial molar free energy and thus also the partial molar entropy of the process. We find that the incorporation of the first three to four water molecules per lipid is exothermic. These water molecules presumably interact directly with oxygen atoms on the phosphate of the lipid head-group. When the first waters have been added the remaining ones are incorporated endothermically. This applies both to the water molecules taken up in the gel phase and in the liquid crystalline state. We also observe that the sorption process triggers a first order phase change from a gel ($L\beta$) to a liquid crystalline ($L\alpha$) phase. For DLPC this occurs at 25°C at a relative humidity of 79% with an endothermic transition enthalpy of 42 ± 2 kJ/mol(DLPC) and for DMPC, 27°C at 93% RH. with $\Delta H=56\pm 5$ kJ/mol(DMPC). We use a previously established model to quantitatively interpret these phase transitions. Furthermore the observed endothermic nature of the sorption process above three to four waters per lipid is fully consistent with the suggestion that the negative free energy of the sorption (swelling) is due to increased thermal excitations and thus a positive entropy. It is more problematic to reconcile the data with models proposing structuring effects in the water as the main cause of the swelling.

As an on-going project we present a study of the water flux through a multibilayer DMPC membrane in the presence of a gradient in water chemical potential, where the gradient is determined by the boundary conditions. The flux was measured as a function of relative humidity in the vapor phase by means of microcalorimetric method described above. When the boundary relative humidity goes above 93% at 27°C, a phase transition from $L\beta$ to $L\alpha$ state is expected along the water activity gradient in accord with the results of the lipid hydration study. This phase transition explains the increase in the lipid membrane permeability observed at $RH>93\%$.

References

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2. L. Wadsö, N. Markova. *Thermochim.Acta.* 2000 (in print).