# Study of Azacrown Ether-Fatty Acid Structure at Organic-Aqueous Interface

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*The adsorption of didodecyl-diazacrown ether and lauric/palmitic acid from toluene solutions on Si(111)-interface was studied by means of neutronreflecivity at AMOR. The azacrown ether at CMC forms either a loosely packed and strongly solvated layer, or"islands", with a thickness of 14 Å, slightly less than the length of fully extended alkyl chains of the alkylated azacrown ether. The mixture of fatty acid and azacrown ether adsorbs on Si(111)-interface in the form of two interpenetrated layers (12+10 Å), supporting our earlier hypothesis of interaction of azacrown ether and fatty acids at interfaces.*

The aim of the current project is to study the adsorption of the mixture of -$C_{10}H_{21}$ substituted azacrown ether (22DD) and lauric or palmitic acid (LAH or PAH, respectively) at the solid-liquid interface. The research is part of our mechanistic studies on the transport of metal ions through Permeation Liquid Membranes. The crucial step for the transport of metal ions is the transfer through the aqueous-organic interface. As a preliminary study we followed the adsorption of the two components from toluene solutions onto the bare Si(111)-interface. In all measurements the concentrations of 22DD and LAH were 0.2 mM (which is equal to the CMC for 22DD, but much less the CMC for LAH.

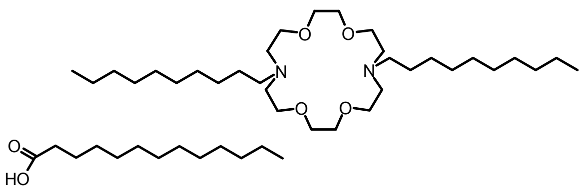


**Figure 1:** Structure of 22DD (above) and LAH (below).

The obtained neutron reflectivity data were analysed using the optical density matrix method as implemented in the software of Parratt32. First the Si(111)-interface was characterised by measuring the reflectivity profiles in water ($H_2O$, $D_2O$) and toluene (toluene-$d_8$). The data received are consistent with a model assuming the presence of a $SiO_2$ layer of 15 Å, which is penetrable by water ($H_2O$, $D_2O$). The thickness of 15 Å of such a $SiO_2$ layer is in agreement with literature values (14-20 Å). The organic solvent of toluene cannot penetrate the $SiO_2$ layer present due to the high hydrophilicity of the solid interface.

In Fig. 2 an exemplary reflectivity curve for 22DD at the Si/toluene-$d_8$ interface is shown. The solid line represents the fitted curve. All our data could be fitted to a model assuming an adsorption of 22DD as a single layer of 14 Å thickness. The layer is not densely packed, but rather strongly penetrated by the solvent. The thickness of that layer is approximately equal to the length of the extended alkyl chains of 22DD in a monolayer, but could also correspond to a strongly interpenetrated bilayer structure of 22DD. When only fatty acid is present in the solution, the layer is not formed, but from the 1:1 mixture with 22DD a layer more densely packed than from pure 22DD seems to be formed (10 Å thickness). This effect on the adsorption of azacrown ether to an interface originates probably from the formation of a 22DD-LAH complex. Earlier results of our studies suggested that the affinity of LAH to 22DD drives the former to the interface. This is confirmed by the present studies. In addition, a thin less dense packed layer of the fatty acid adsorbs on top of the first layer (12 Å thickness), probably also due to the formation of the complex with 22DD. Further studies will be necessary to evaluate the exact composition of the layers formed.

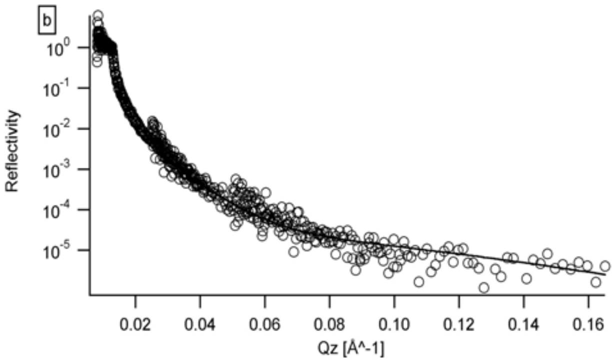


**Figure 2:** Neutron reflectivity profile for 22DD at Si/ toluene-$d_8$ solid/liquid interface.

As mentioned above the main system of interest for our research is the aqueous-organic liquid-liquid interface of water and toluene. We have performed some initial preliminary experiments to study such an interface by neutron reflectometry testing an air/toluene/water system. As the significant absorption of neutrons passing through the top toluene layer has to be avoided the thickness of this layer has to be reduced to a few µm. So far we have not obtained such a thin layer of toluene on water due to the very high contact angle for toluene on water. We believe however that the problem can be circumvented by a proper design of the experimental set-up, which will be the subject of further studies.

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