Experimental report

20/06/2022

Proposal:	**9-10-1662**	**Council:**	4/2020

Title: Molecular origin of “kyu-kyu” in detergency: Composition of SDS/DDAO mixed micelles and interfacial layers

Research area: Soft condensed matter

This proposal is a new proposal

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Samples:
SDS
DDAO

Instrument	Requested days	Allocated days	From	To
D33	3	2	27/03/2021	29/03/2021
FIGARO	3	2	12/07/2021	14/07/2021
D11	3	0		

Abstract:

In the context of dishwashing, the acoustic emissions derived by the physical contact of the human fingertip across a wet lubricated surface (or dish) are defined by the Japanese term, ‘kyu-kyu’. These ‘kyu-kyu’ or squeaking sounds, indicative of customer satisfaction of a cleaned surface, have their origin in a physical phenomenon known as stick-slip friction. We hypothesize that this stick-slip, facilitated by the presence of a detergent, is caused in part by disruption of the surfactant bilayer absorbed to the contacting surface as rinsing occurs. The friction force may be mediated by the presence of mixed micelles, polymer additives, soils and skin lipids (Fig. 1). Here as the first step of a 4-year PhD project in collaboration with P&G, we propose a combined small-angle neutron scattering (SANS) and neutron reflectivity (NR) study of the self-assembled structures in solution and at interfaces formed by two surfactants. The surfactants, SDS and DDAO (dodecyldimethylamine oxide) are analogues of the surfactants used in the P&G formulation and widely reported to exhibit significant synergy, forming mixed micelles of compositionally dependent structure.

Experiment Objectives:

In the context of dishwashing, the acoustic emissions derived by the physical contact of the fingertip across a wet lubricated surface are defined by the term '*kyu-kyu*' and represent a customer satisfaction criterion. These squeaking sounds take their origin in the physical phenomenon of stick-slip friction and are hypothesized to result from the partial disruption of adsorbed surfactant bilayers on mechanical contact whilst rinsing occurs. The frictional force may be mediated by the presence of mixed micelles, polymer additives, soils, and skin lipids. Here, in collaboration with P&G, we propose a neutron reflectivity (NR) study of skin lipids at the air-water interface, including cholesterol, ceramide C24 NS, and lignoceric acid (Figure 1). We will vary the composition of the lipid monolayers to investigate the influence of free fatty acid inclusion, and the monolayer formation on subphases of D_2O, and D_2O and PBS buffer, at varying surface pressures. In addition, we propose a small-angle neutron scattering (SANS) study into the architecture of skin lipid liposomes comprising cholesterol, ceramide C24 NS, lignoceric acid, and palmitic acid of varying composition. We propose to investigate their interaction with the deuterated surfactant, d-SDS, and the influence of temperature on these systems as it is know that ceramide possesses a phase transition temperature at 90 °C. These studies are complementary and will provide insight into the interactions between a simplified skin model and the surfactants which typify the dishwashing system.

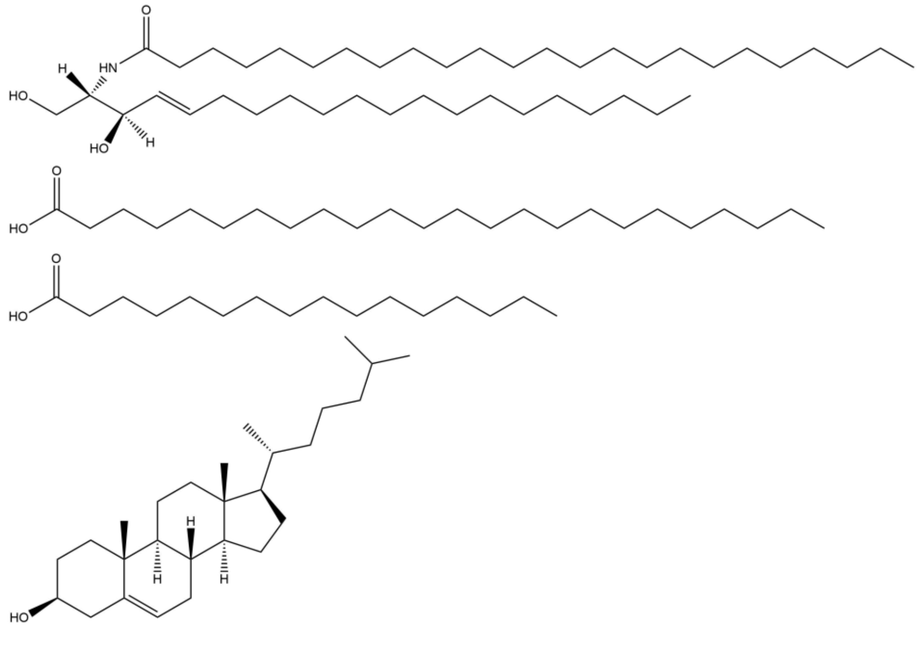

Figure 1: From top to bottom the chemical structures of ceramide C24 NS, lignoceric acid, palmitic acid and cholesterol, respectively.

Experiment Report:

The measurements at both FIGARO and D33 were performed remotely. During the time at D33, measurements were taken to characterize the bulk structure of skin lipids and surfactants in D_2O, for example: Cer:Chol:LA (1:1:3) and d-SDS, and SDS:DDAO (1:1). These measurements were performed at different temperatures as ceramide is known to posses a phase transition temperature approaching 90 °C. These results will be used in conjunction with the

NR data to characterize the system and provide insight into the skin lipid vesicle/monolayer compositions and their interaction with common surfactants.

Initial analysis of the data obtained from D33 involved plotting the raw intensity against Q in order to examine the influence of temperature on the structure of surfactant micelles. Figure 1 is an example of the data obtained for d-SDS, and d-SDS with DDAO in a 1:1 molar ratio where scattering intensity appears to be affected by increasing temperature.

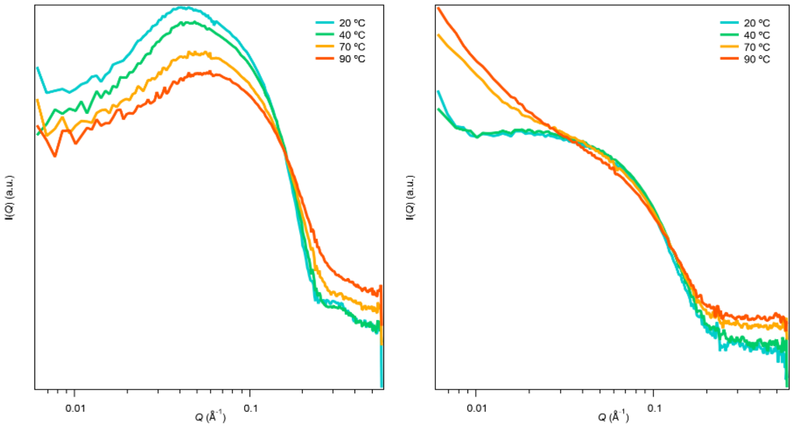

Figure 1: (left) Raw SANS data of 25 mM d-SDS at various temperatures as indicated by the legend, (right) raw SANS data of d-SDS:DDAO (1:1)

Further studies were carried out on ceramide:cholesterol:fatty acid compositions at various temperatures in order to investigate the influence on structure and to compare the structure obtained on the inclusion of either fatty acid; palmitic and lignoceric acid, and their interactions with d-SDS (Figure 2).

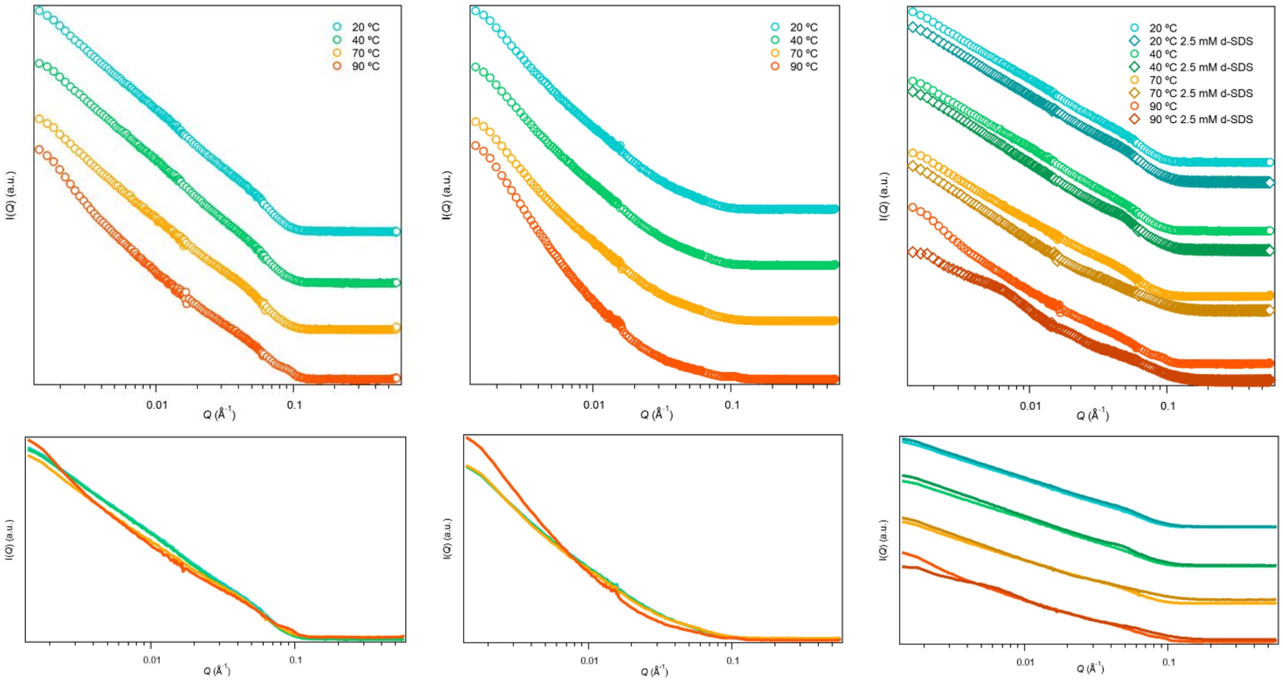

Figure 2: Raw SANS data of ceramide:cholesterol and either fatty acid, and the interaction of the skin lipids with 25 mM d-SDS; (top) The full data set for each sample, (bottom) the full data set with scans not offset. Progressing left to right: ceramide:cholesterol:**lignoceric acid**, ceramide:cholesterol:**palmitic acid**, cer:chol:la and **25 mM d-SDS**.

The most notable alteration in structure is observed at 90 °C for each sample, at which temperature ceramide is known to possess a phase transition temperature. Little structural change is observed on increasing temperature from 20 to 40 °C for both skin lipids and surfactants alike.

During the time at FIGARO, measurements were taken to characterise the surface structure of ceramide:cholesterol, and ceramide:cholesterol:lignoceric acid monolayers at the air-water interface. The monolayers were deposited on both D_2O and D_2O-PBS subphases as LB trough measurements have shown differences in the Π-A isotherms of these monolayers on these subphases. Figure 3 is an examples of ceramide:cholesterol:lignoceric acid monolayers on D_2O and D_2O-PBS subphases.

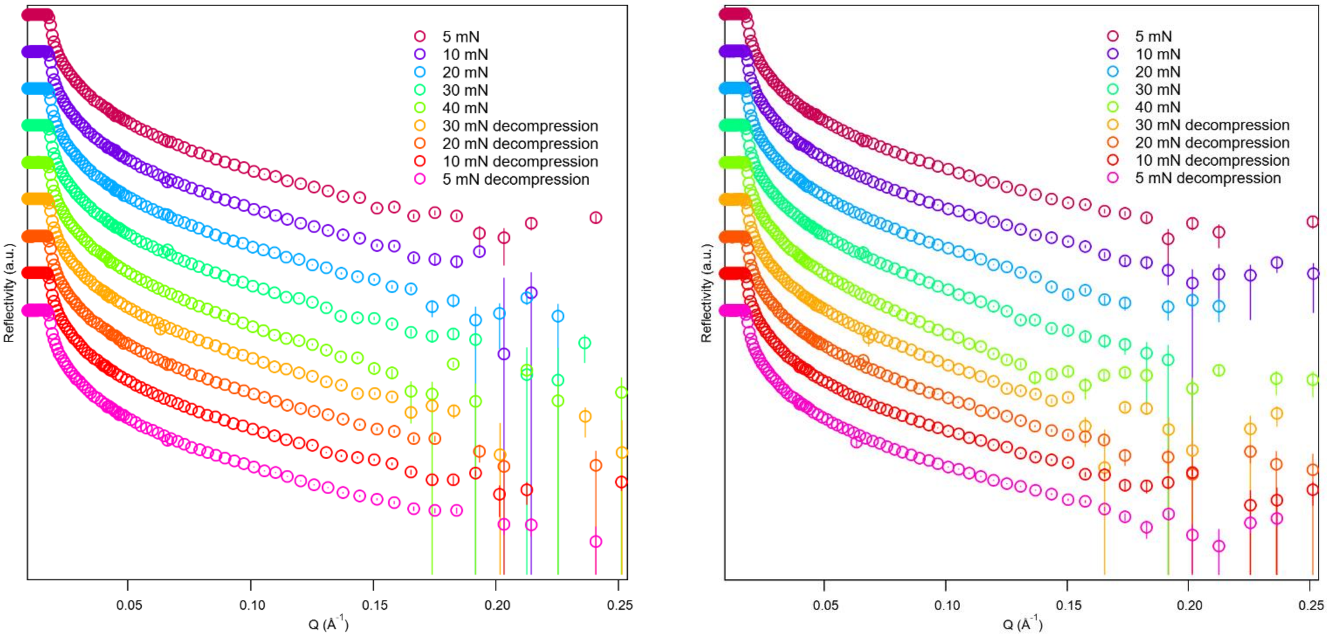

Figure 3: (left) ceramide:cholesterol:lignoceric acid monolayers deposited on D_2O, (right) ceramide:cholesterol:lignoceric acid monolayers on D_2O-PBS, each as a function of surface pressure.

While NR measurements appear featureless, initial fitting indicates the presence of a monolayer of ~40 nm. The thickness of the monolayer is shown to increase with the inclusion of lignoceric acid, an expected observation due to the chain length of the fatty acid. The monolayers dispersed on the subphase containing PBS are also shown to vary slightly compared to those prepared on D_2O alone.