Experimental report

29/08/2024

Proposal: **9-10-1740** **Council:** 10/2022

Title: Structure of interfacial layers insuperspreading films

Research area: Soft condensed matter

This proposal is a new proposal

Main proposer: **Emanuel SCHNECK**

Experimental team: Joshua REED
Seforah Carolina MARQUES SILVA
Emanuel SCHNECK
Joachim VENZMER
Tatiana GAMBARYAN-ROISMAN

Local contacts: Philipp GUTFREUND
Samantha MICCIULLA

Samples: Break-Thru S233
Break-Thru S240

Instrument	Requested days	Allocated days	From	To
FIGARO	3	3	10/04/2023	13/04/2023

Abstract:

We intend to use specular neutron reflectometry (NR) to investigate the structure of interfacial surfactant layers involved in the phenomenon of superspreading (no connection to superspreading in the context of infectious diseases) in order to distinguish between different scenarios that have remained highly debated in the literature. We are going to work with non-superspreading and superspreading versions of trisiloxanes, Break-Thru S 233 and Break-Thru S 240, respectively (both by Evonik), and with solid surfaces of two different levels of hydrophobicity.

Experimental Report
Title: Structure of interfacial layers in superspreading films
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Experimental Team: Joshua Reed, Séforah Carolina Marques Silva, Philipp Gutfreund, Joachim Venzmer, Tatiana Gambaryan-Roisman, Emanuel Schneck

Background

Superspreading surfactants cause very small amounts of water to spread across large radii on hydrophobic surfaces (Fig.1A). This effect is caused by a reduction in free energy of the system when spreading occurs, which is quantifiable by a spreading coefficient that depends on the surface tension (or energy) of each of the three interfaces, solid-air, liquid-air, and solid-liquid [2]. The first two of these are easily measurable whereas the interfacial energy of the solid-liquid interface is more complicated to measure.

Our experiments dealt with two trisiloxane surfactants, a normal non-superspreading surfactant (Break Thru® S233) and a superspreading surfactant (Break Thru® S240), both from Evonik, Essen, Germany. They both consist of a trisiloxane group with a small polymer chain (Fig. 1B). The similarity of these molecules means that both surfactants have almost identical surface tensions and when spread on the same hydrophobic surface, the main cause of a difference in the spreading ability (directly from the spreading coefficient) is the interfacial energy of the solid-liquid interface. Therefore to determine the specific causes of the differences in spreading, a study of the solid-liquid interface, as was done here, is important.

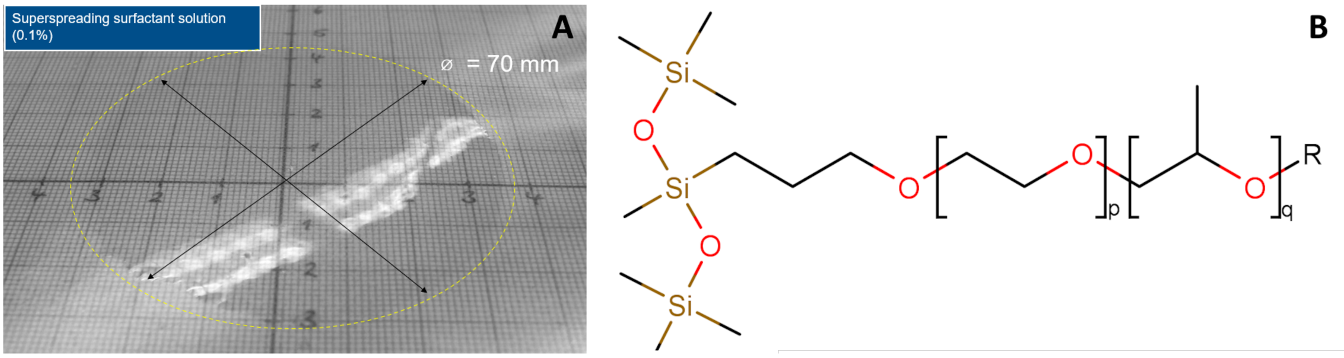

Figure 1: **A:** 50 μl 0.1% solution of superspreading surfactant in water on a hydrophobic polypropene surface. **B:** Chemical structure of Break Thru® S233 (p = 10, q = 2, non-superspreading) and S240 (p = 6, q = 3, superspreading)

Experimental

The experimental aim was to investigate the surfactant molecular behaviour at the interfaces using neutron reflectometry (NR) using 3 days of beam time on the instrument FIGARO. The experimental set-up involved using a custom acrylic cell designed to have externally heated water/D_2O reservoirs within a sealable environment holding a hydrophobic silanised silicon block. The water baths were gently heated to increase the relative humidity inside the cell at ambient temperature (to prevent instantaneous drying through evaporation during superspreading), and then a surfactant solution was deposited onto the block. Measurements were done on non-superspreading 0.1% S233 solutions and superspreading 0.1% S240 solutions, both in D_2O. Solutions using D_2O were chosen to provide contrast to the surfactant molecules. Additional data at the air-water interface were also measured using the same 0.1% solutions of surfactants on a Langmuir trough set-up.

Results

A majority of the data showed a disconnect between the reflectivity curves obtained with the two incident angles used. This can be attributed to beam attenuation affecting the reflection of a second interface (in this case, liquid-air) when measuring thin films of thicknesses of several μm to several tens of μm. Attenuation depends on path length and hence incident angle, leading to a more attenuated back-side reflection at smaller angles. As a solution to deal with this, fitting was split into the two angles which included attenuation calculations but were still done simultaneously.
Analysis started with a S240 system which did not exhibit the disconnect between the two angles, because the addition of 200 μl D_2O led to a macroscopically thick liquid film. Shown in Fig. 2 A and B are the reflectivity curve of this system and the volume fractions of all chemical reconstructed in the spirit of our earlier work [1]. The solid red lines in Fig. 2 are the fits resulting from the associated SLD profiles. To account for the round sample size being smaller than the rectangular beam footprint a fit of the silicon block, the fit included a contribution from the measurement of the bare block in air (Fig. 1 D), which corresponds to the volume fraction profiles in Fig. 1 C.
Looking at the volume fractions in Fig. 2 A, the surfactant, which is split into a hydrophobic trisiloxane part (yellow) and a hydrophilic polymer part (red), shows a complete coverage of the interface with surfactant molecules and the hydrophobic part is essentially water-free.

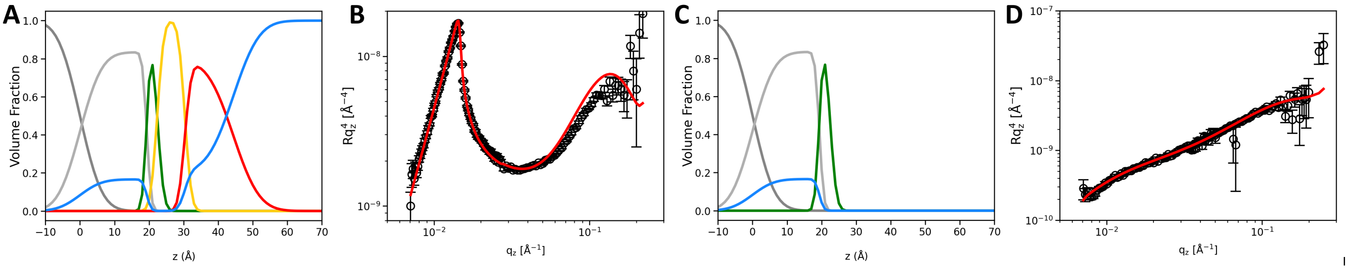

Figure 2: Volume fractions and neutron reflectivity curves of experimental data with solid lines to indicate the simulated reflectivity curves according to the best matching parameters in the model demonstrated by the volume fractions. **A,B:** Non-superspread S240 droplet (200 µl of water added to a superspread puddle of 10 µl 0.1% S240 in water) (Fractions: $\Phi(z)$ of Si (dark grey), SiO_2 (light grey), silane (green), D_2O (blue), trisiloxane (yellow), polymer (red)) **C,D:** Functionalised silicon block with no sample (fractions: $\Phi(z)$ of Si (dark grey), SiO_2 (light grey), silane (green))

Fig. 3 B shows the fitted reflectivity for a superspread layer, taking into account attenuation effects. Here the reconstructed volume fractions (Fig. 3 A) agree with those in Fig. 2 A, supporting the analytical methodology.
Non-superspreader (S233) data was analysed in the same way as above because curiously it also showed thin layer attenuation. We hypothesise that this is because of the much larger amount of solution needed to measure, as no superspreading occurs, some contact with the edge of the cell and/or o-rings caused a meniscus pulling liquid away from the center of the puddle, creating a thin enough layer for the attenuated back-reflection to be seen. This data is shown in Fig. 3 D, which shows a major difference in hydration of the interface between the two surfactants. There is considerably less volume of non-superspreading S233 surfactant at the solid interface, and the hydrophobic part of the molecule exhibits significant hydration. This result is likely related to different spreading coefficients because the contact of the polar water (in this case D_2O) with the hydrophobic substrate will increase the interfacial energy. The less amount of S233 molecules at the interface, presumably due to inefficient packing, is the main difference from the tighter packing of the superspreading S240 surfactant which has no hydration at the solid-liquid interface and thus a lower interfacial energy. The explanation of this difference could lie in the length of the polymer chains, as S230 has a chain that is relatively longer and may create some steric hindrance between molecules.

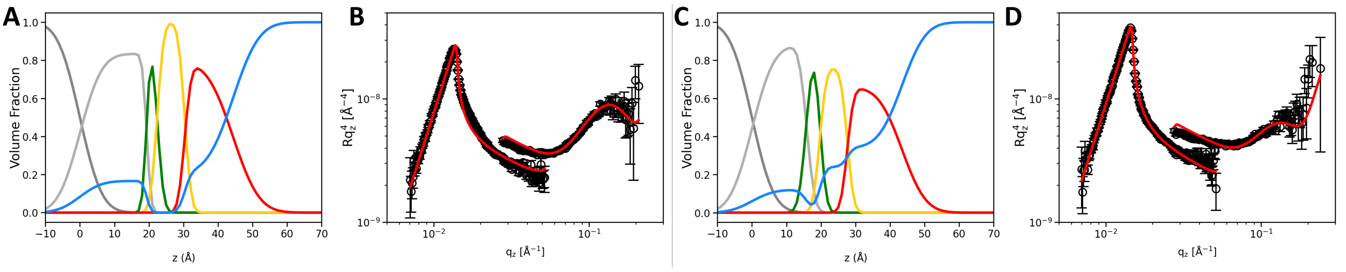

Figure 3: Volume fractions and neutron reflectivity curves of experimental data with solid lines to indicate the simulated reflectivity curves (showing clearly the attenuation affects) according to the best matching parameters in the model demonstrated by the volume fractions. **A,B:** Superspread S240 (0.1% 10 µl) **C,D:** S233 (0.1% 200 µl) (Fractions: $\Phi(z)$ of Si (dark grey), SiO_2 (light grey), silane (green), D_2O (blue), trisiloxane (yellow), polymer (red))

References

[1] Samantha Micciulla, Yuri Gerelli, Richard A Campbell, and Emanuel Schneck. A versatile method for the distance-dependent structural characterization of interacting soft interfaces by neutron reflectometry. *Langmuir*, 34(3):789–800, 2018.

[2] Joachim Venzmer. Superspreading — 20years of physicochemical research. *Curr. Opin. Colloid Interface Sci.*, 16(4):335–343, August 2011.