# Experimental report

17/04/2020

**Proposal:** 9-10-1615 **Council:** 10/2019

**Title:** Bending Moduli of CO2 Containing Surfactants in Oil-in-Water (O/W) Microemulsions

**Research area:** Soft condensed matter

**This proposal is a new proposal**


**Main proposer:** Michael GRADZIELSKI

**Experimental team:** Rahel MARSCHALL

**Local contacts:** Sylvain PREVOST


**Samples:** C16H33(C2H4O)9(CO2)3
C12H25(C2H4O)9(CO2)3

| Instrument | Requested days | Allocated days | From | To |
|---|---|---|---|---|
| D33 | 1 | 1 | | |
| IN15 | 3 | 2 | 28/01/2020 | 30/01/2020 |
| D11 | 0 | 1 | 02/02/2020 | 03/02/2020 |


## Abstract:

Aim of this proposal is to determine the bending moduli of the monolayer of nonionic surfactants containing different amounts of CO2 in their hydrophilic head group at the oil/water interface. This will be done by a combination of NSE and SANS on oil-in-water (O/W) microemulsions in D2O that are saturated with d22-decane in order to have a film contrast. Under these conditions combining NSE and SANS allows uniquely to determine both mean and saddle-splay modulus. This is very interesting as the CO2 containing surfactants deviate systematically from the conventional EO surfactants with respect to their phase behaviour but also with respect to the solubilisation properties. With increasing CO2 content in the head group the solubilisation capacity is largely enhanced. According to standard theory this should be reflected in correspondingly changed values of the bending moduli. However, so far no experimental evidence exist and NSE and SANS will allow to obtain such information much more directly and with a much higher precision, than possible with any other method. Such information will be essential to enable optimised formulations with these novel surfactants.

**Bending Moduli of CO2 Containing Surfactants in Oil-in-Water (O/W) Microemulsions**

Experimental report for experiment 9-10-1615 at IN15 (Jan. 28–30, 2020)
Berlin, April 17, 2020

The aim of this proposal was to determine the bending moduli of the monolayer of nonionic surfactants containing different amounts of $CO_2$ in their hydrophilic head group at the oil/water interface. This has been done by a combination of NSE and SANS on oil-in-water (O/W) microemulsions in $D_2O$ that are saturated with $D_{22}$-decane in order to have a film contrast. Under these conditions combining NSE and SANS allows uniquely to determine both mean and saddle-splay modulus. This is very interesting as the $CO_2$ containing surfactants deviate systematically from the conventional EO surfactants with respect to their phase behaviour but also with respect to the solubilisation properties. With increasing $CO_2$ content in the headgroup the solubilisation capacity is largely enhanced. According to standard theory this should be reflected in correspondingly changed values of the bending moduli. Such information will be essential to understand the effect of $CO_2$ incorporation on the properties of amphiphilic monolayers and to enable optimised formulations with these novel surfactants.

Experimental setup and samples

For this experiment we prepared microemulsions in film contrast (see Table 1). Therefore, we used deuterated decane. 50 mM of six different surfactants in $D_2O$ were saturated with $D_{22}$-decane. For four samples also 80 mM geraniol was added, to extend the system to one containing a cosurfactant. Afterwards the solutions were shaken and 5 days equilibrated. The NSE data were carried out on IN15 with 5 mm cuvettes. Additionally, in-situ DLS was measured. The SANS measurements were carried out on D11 and were measured at 1.4 m and 8 m at 4.5 Å in 2 mm cuvettes. All measurements were carried out at 25°C.

*Table 1: Overview of the samples measured by NSE and SANS. MAR211 and MAR212 are only measured by SANS.*

| Label | Long name | Surfactant | c(surfactants) \mM | c(geraniol) \mM | c($D_{22}$-decane) \mM |
|---|---|---|---|---|---|
| MAR200 | DT_C120.0_dD100 | $C_{12}(EO)_{14}$ | 50 | - | 100 |
| MAR201 | DT_C121.3_dD100 | $C_{12}(EO)_{11.4}(CO_2)_{1.3}$ | 50 | - | 100 |
| MAR203 | DT_C123.1_dD100 | $C_{12}(EO)_{8.2}(CO_2)_{3.1}$ | 50 | - | 100 |
| MAR204 | DT_C160.0_dD100 | $C_{16}(EO)_{14.6}$ | 50 | - | 100 |
| MAR205 | DT_C161.5_dD100 | $C_{16}(EO)_{9.3}(CO_2)_{1.5}$ | 50 | - | 100 |
| MAR206 | DT_C162.8_dD100 | $C_{16}(EO)_{7.8}(CO_2)_{2.8}$ | 50 | - | 100 |
| MAR207 | DTOC_C120.0_G80_dD200 | $C_{12}(EO)_{14}$ | 50 | 80 | 200 |
| MAR208 | DTOC_C121.3_G80_dD200 | $C_{12}(EO)_{11.4}(CO_2)_{1.3}$ | 50 | 80 | 200 |
| MAR209 | DTOC_C123.1_G80_dD200 | $C_{12}(EO)_{8.2}(CO_2)_{3.1}$ | 50 | 80 | 200 |
| MAR210 | DTOC_C160.0_G80_dD200 | $C_{16}(EO)_{14.6}$ | 50 | 80 | 200 |
| MAR211 | DTOC_C161.5_G80_dD200 | $C_{16}(EO)_{9.3}(CO_2)_{1.5}$ | 50 | 80 | 200 |
| MAR212 | DTOC_C162.8_G80_dD200 | $C_{16}(EO)_{7.8}(CO_2)_{2.8}$ | 50 | 80 | 200 |

Data

In Figure 1-Figure 10 the raw data is plotted as the intensity corrected by the resolution over the delay time.

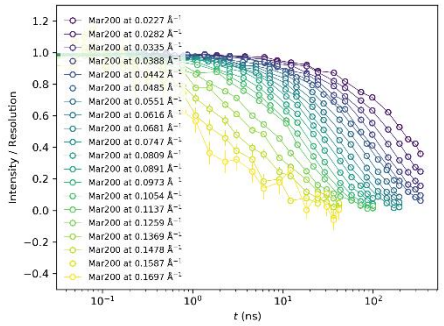


*Figure 1: NSE data $C_{12}$-reference sample with 100 mM $D_{22}$-decane.*

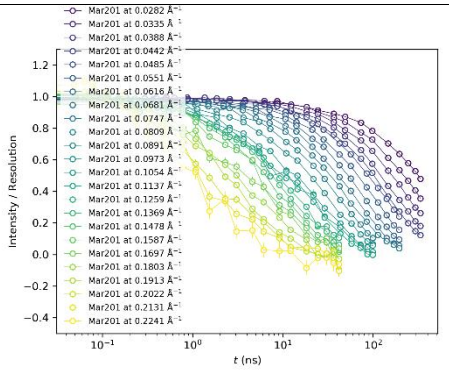


*Figure 2: NSE data $C_{12}$-surfactant with 1.3 $CO_2$-units and 100 mM $D_{22}$-decane.*

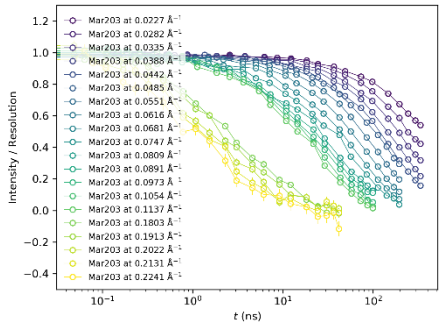


*Figure 3: NSE data $C_{12}$-surfactant with 3.1 $CO_2$-units and 100 mM $D_{22}$-decane.*

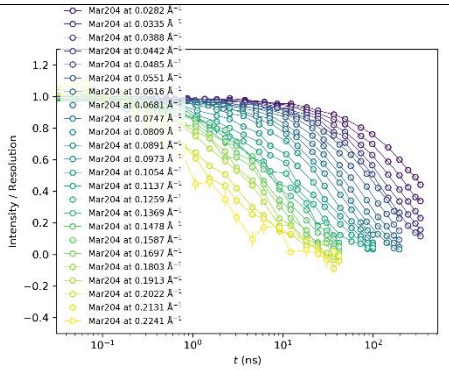


*Figure 4: NSE data $C_{16}$-reference sample with 100 mM $D_{22}$-decane.*

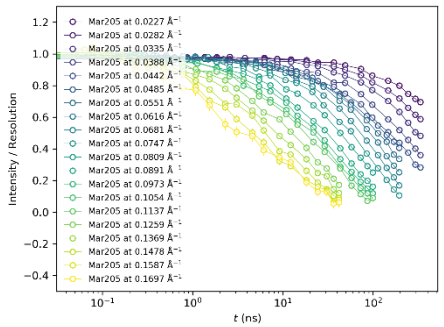


*Figure 5: NSE data $C_{16}$-surfactant with 1.5 $CO_2$-units and 100 mM $D_{22}$-decane.*

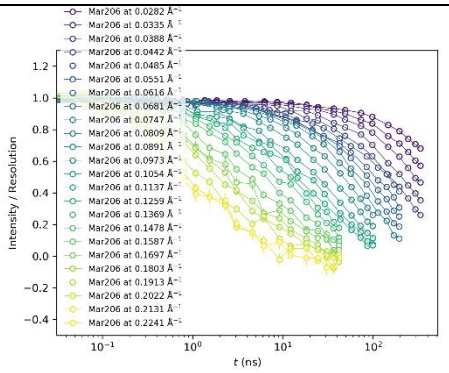


*Figure 6: NSE data $C_{16}$-surfactant with 2.8 $CO_2$-units and 100 mM $D_{22}$-decane.*

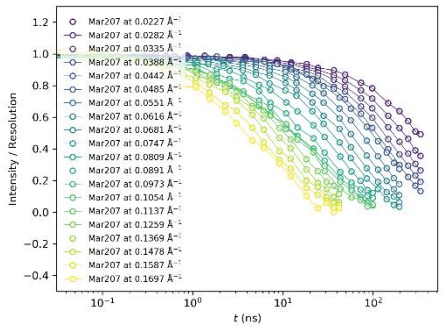


*Figure 7: NSE data $C_{12}$-reference sample with 200 mM $D_{22}$-decane and 80 mM geraniol.*

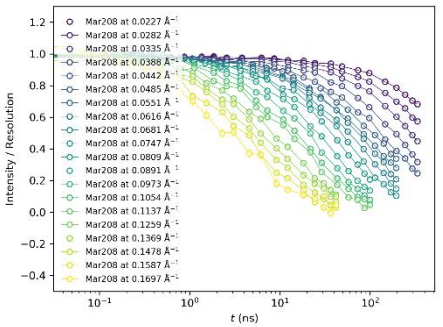


*Figure 8: NSE data $C_{12}$-surfactant with 1.3 $CO_2$-units with 200 mM $D_{22}$-decane and 80 mM geraniol.*

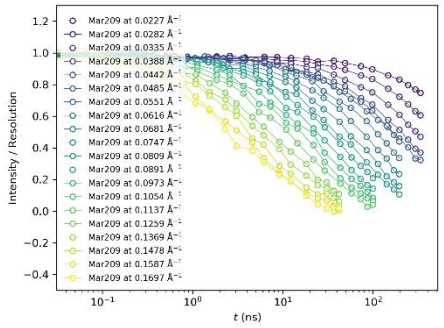


*Figure 9: NSE data $C_{12}$-surfactant with 3.1 $CO_2$-units with 200 mM $D_{22}$-decane and 80 mM geraniol.*

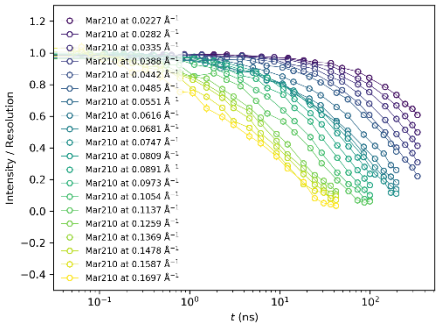


*Figure 10: NSE data $C_{16}$-reference sample with 200 mM $D_{22}$-decane and 80 mM geraniol.*

The scattering data from SANS are plotted in Figure 11 and Figure 12. Figure 11 shows the samples without geraniol and Figure 12 the data with geraniol. It can be seen that the addition of oil and geraniol both leads to increasing micelle size and that those effects are increasing with increasing $CO_2$ content. The $C_{16}$-samples were hard to handle and have to be discussed carefully.

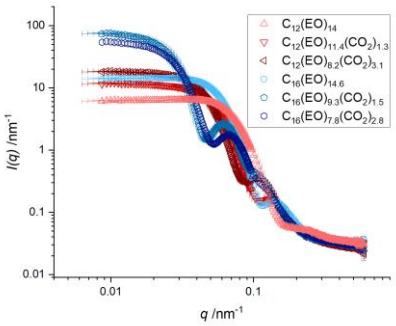


*Figure 11: SANS data of samples with 100 mM $D_{22}$-decane and without geraniol.*

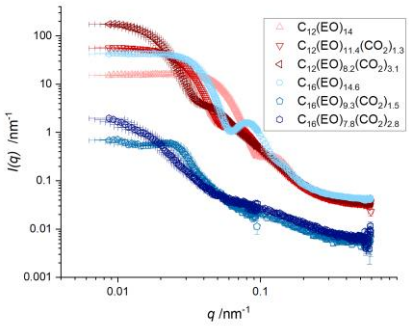


*Figure 12: SANS data of samples with 200 mM $D_{22}$-decane and with 80 mM geraniol.*

<u>Data analysis</u>

To evaluate the experimental data a Zilman-Granek model was used (see Figure 13), which shows poor results. In following studies the experimental data will be fitted with Milner-Safran model to improve the results and to obtain detail parameter of the bending moduli. We assume to see that the corona of the $CO_2$ containing systems is more flexible than the $CO_2$ free systems. Previous studies lead to the conclusion that the $CO_2$ free corona binds water stronger than the $CO_2$ containing.

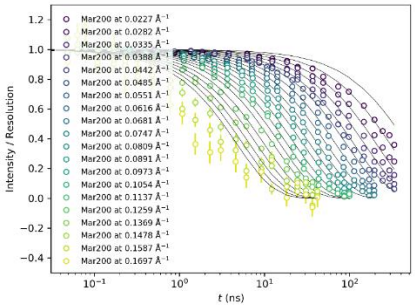


*Figure 13: Example of data fitted with the Zilman-Granek model (here sample MAR200).*