Experimental report

31/10/2023

Proposal: **EASY-1081** **Council:** 10/2022

Title: Understanding and controlling the high viscoelasticity of alfa-cyclodextrin/surfactant films at the air/water interface - data completion

Research area: Materials

This proposal is a new proposal

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Samples: alfa-cyclodextrin

Instrument	Requested days	Allocated days	From	To
FIGARO	24	24	22/06/2023	23/06/2023

Abstract:

We have published articles over the last years on the highly viscoelasticity in cyclodextrin/surfactant films at the air/water interface, and low-Qz measurements of the film composition using neutron reflectometry (NR) have started to provide a key contribution in understanding its origin. We performed experiment #9-10-1622 on FIGARO in September 2021 but delays in the despatch of one surfactant meant that the dataset remained incomplete. Even so, initial data hinted at a breakthrough in understanding the viscoelasticity in cyclodextrin films with surfactant mixtures for the first time. This experiment is proposed to complete the low-Qz dataset including repeats that are necessary for data validation, and extend the dataset to full-Qz measurements of the structure for the most viscoelastic films. Such an experiment was accepted on INTER at ISIS in December 2021, but facility downtime meant that the scheduled experiment was cancelled. FIGARO is by far the most appropriate instrument for this work due to its excellent at low-Qz, and the instrument responsible (Dr. Gutfreund) is supportive of this application for us to complete this work instead on FIGARO for immediate publication.

PRELIMINARY EXPERIMENTAL REPORT: EASY-1081

Understanding and controlling the high viscoelasticity of alfa-cyclodextrin/surfactant films at the air/water interface - data completion

Richard Campbell & Daniel Ondo, FIGARO, 22–23 June 2023

Abstract

We have published articles over the last years on the highly viscoelasticity in cyclodextrin/surfactant films at the air/water interface, and low-Qz measurements of the film composition using neutron reflectometry (NR) have started to provide a key contribution in understanding its origin. We performed experiment #9-10-1622 on FIGARO in September 2021 but delays in the despatch of one surfactant meant that the dataset remained incomplete. Even so, initial data hinted at a breakthrough in understanding the viscoelasticity in cyclodextrin films with surfactant mixtures for the first time. This experiment is proposed to complete the low-Qz dataset including repeats that are necessary for data validation, and extend the dataset to full Qz measurements of the structure for the most viscoelastic films. Such an experiment was accepted on INTER at ISIS in December 2021, but facility downtime meant that the scheduled experiment was cancelled. FIGARO is by far the most appropriate instrument for this work due to its excellent at low-Qz, and the instrument responsible (Dr. Gutfreund) is supportive of this application for us to complete this work instead on FIGARO for immediate publication.

Experimental Methodology & Approach

The plan involved making:

- 600 g ACMW
- 70 ml x 30 mM aCD/D2O
- 180 ml x 30 mM aCD/ACMW
- 50 ml x 10.2 mM hC12/D2O
- 80 ml x 10.2 mM hC12/ACMW
- 25 ml x 10.2 mM dC12/D2O
- 100 ml x 10.2 mM dC12/ACMW
- 25 ml x 4.00 mM hC14/D2O - stock solution for diluting to different concentrations
- 75 ml x 4.00 mM hC14/ACMW - stock solution for diluting to different concentrations
- 25 ml x 4.00 mM dC14/D2O - stock solution for diluting to different concentrations
- 25 ml x 4.00 mM dC14/ACMW - stock solution for diluting to different concentrations

References molecular weights:

The first experimental report states "10.701 g of aCD in 330 ml of ACMW" = 30 mM, so from this the aCD molecular weight including 10% water is 1080.91 g/mol. We should use this reference value for consistency between the datasets.

Also, for the surfactants (SDS abbreviated to C12 and STS abbreviated to C14), we have:

- hC12 = 288.38 g/mol
- dC12 = 313.38 g/mol
- hC14 = 316.43 g/mol
- dC14 = 345.43 g/mol

The C12 concentrations that were measured previously are:

A = 0.6 mM
B = 0.9 mM
C = 1.3 mM
D = 1.74 mM
E = 2.0 mM
F = 2.8 mM
G = 3.4 mM

We made enough solutions to allow making any of the following 22 samples. The best-case scenario was to measure 20 samples and if it had not been possible it would have been 16 samples. The extended surfactant structure above the viscoelasticity maximum was certainly worth measuring to resolve directly not only what structure switches the viscoelastic effect on (1.3 mM), but also what structure switches the effect off (2.8 mM). In that case, here are the 22 x 30-ml samples that we aimed to be in a position to make during the experiment:

FULL-Q = 6 in D2O, 1.3/2.8 mM for aCD/hC12/hC14, aCD/dC12/hC14 and aCD/hC12/dC14**
FULL-Q = 2 in ACMW, 1.3/2.8 mM for aCD/dC12/dC14/ACMW
LOW-Q = 7 in ACMW, 0.6/0.9/1.3/1.74/2.0**/2.8/3.4* for aCD/hC12/hC14
LOW-Q = 7 in ACMW, 0.6/0.9/1.3/1.74/2.0**/2.8/3.4* for aCD/dC12/hC14

The reason for 22 samples is that, in principle, only 1 additional contrast is necessary for the compositional analysis, but it was not clear at the outset which one that was. So if during the experiment it has been clear that one of the two contrasts was not useful, we could have skipped several samples. If not, and if we could have measured 20 samples and then skipped the highest concentration sample from the compositional analysis (3.4 mM*) on the basis that the compositions of the three highest concentrations look similar. Then if we could have measured only 16 samples, we could have skipped the ones marked ** leaving 3 full-Q contrasts for viscoelasticity-ON and viscoelasticity-OFF as well as 5 points on the compositional isotherm (skipping 2 of the 3 points that look almost the same). Scientifically, this seems like a robust plan, and the order of the experiments was chosen to give the most flexibility to the outcome.

Each sample requires the mixing in new Falcon tubes of:

10 ml of 30 mM aCD
10 ml of 10.2 mM C12
10 ml of 3 x intended concentration of C14

- followed by aspiration in the Falcon tubes to the required volume for pouring into the troughs.

Here are the solutions to be made:

ACMW made by weight:

--> MAKE-1: 600 g ACMW in a 1 litre flask = 53.94 g D2O and 546.06 g H2O

Total volume for 30 mM aCD:
--> MAKE-2: aCD/D2O = 6 x 10 ml = 60 ml --> make 70 ml = 2.270 g
--> MAKE-3: aCD/ACMW = 16 x 10 ml = 160 ml --> make 180 ml = 5.837 g

Total volume for 10.2 mM hC12:
--> MAKE-4: hC12/D2O = 4 x 10 ml = 40 ml --> make 50 ml = 147.1 mg
--> MAKE-5: hC12/ACMW = 7 x 10 ml = 70 ml --> make 80 ml = 235.3 mg

Total volume for 10.2 mM dC12:
--> MAKE-6: dC12/D2O = 2 x 10 ml = 20 ml --> make 25 ml = 79.9 mg
--> MAKE-7: dC12/ACMW = 9 x 10 ml = 90 ml --> make 100 ml = 319.6 mg

Total concentration for 10 ml hC14:
--> MAKE-8: hC14/D2O = 1.3+1.3+2.8+2.8 mM = 8.2 mM --> round to 10 mM --> make stock with 31.6 mg --> dilute 25 ml = 4.00 mM
--> MAKE-9: hC14/ACMW = 2 x (0.6+0.9+1.3+1.74+2.0+2.8+3.4) mM = 25.48 mM --> round to 30 mM --> make stock with 94.9 mg --> dilute 75 ml = 4.00 mM

Total concentration for 10 ml dC14:
--> MAKE-10: dC14/D2O = 1.3+2.8 mM = 4.1 mM --> round to 10 mM --> make stock with 34.5 mg --> dilute to 25 mL = 4.00 mM
--> MAKE-11: dC14/ACMW = 1.3+2.8 mM = 4.1 mM --> round to 10 mM --> make stock with 34.5 mg --> dilute to 25 ml = 4.00 mM

Summary & Outlook

The experimental plan was completed in full, and an excellent dataset was achieved. Indeed, the number of measurements made exceeded our expectations as a result of highly efficient sample changes. The initial data analysis is underway and is looking very positive: the composition analysis should be completed in November 2023 and the initial structural analysis hints at a surprising result. It appears that the most viscoelastic film has a surfactant monolayer with several multilayers of aCD/surfactant complexes beneath. We knew already from the previous compositional analysis that the structure is not a simple monolayer of complexes. The maximum coverage of any complexes layer is 45%. So it appears to be a network structure, as if there are gaps the viscoelasticity would be unlikely to be so high. It appears also from the first fitting results that the C12 surfactant is dominating the interface over the C14 surfactant. A further inference is that isotope effects are in effect in the complex layers. A first reaction could be that this is unfortunate, but there was a recent paper published relating such information to the underlying driving force for self-assembly in polyelectrolyte/surfactant mixtures, so as a collaboration, we are open to learning a lot of information from these data about the underlying driving forces in the self-assembly for these systems. The aim is to complete the full data analysis this year (composition by the end of November 2023 and structure by the end of December 2023) so that the results can be included in a manuscript for publication early in 2024.