Experimental report

27/08/2023

Proposal:	**9-10-1622**	**Council:**	10/2019
Title:	Understanding and control of highly viscoelastic films composed 2:1 alpha-cyclodextrin/surfactant inclusion complexes		
Research area:	Soft condensed matter		

This proposal is a new proposal

Main proposer:	**Richard CAMPBELL**
Experimental team:	José CAMPOS TERAN Daniel ONDO Yixuan YAN Richard CAMPBELL Glenn COOPE
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Samples:	Sodium Dodecyl Sulfate Alpha-cyclodextrin Dodecyltrimethylammonium Bromide Sodium octyl sulfate ($C_8H_{17}SO_4Na$) sodium tetradecyl sulfate / $C_{14}H_{29}NaO_4S$ d17-sodium octyl sulfate D25-Sodium Dodecyl Sulfate d29-sodium tetradecyl sulfate d25-dodecyltrimethylammonium bromide d25-sodium dodecyl sulfonate sodium dodecyl sulfonate

Instrument	Requested days	Allocated days	From	To
FIGARO	4	2	21/09/2021	23/09/2021

Abstract:

Alpha-cyclodextrin (aCD)/surfactant solutions spontaneously form highly viscoelastic films at the water/air interface. We have investigated these films over the last decade with the aims of understanding and controlling their behavior in order to design new functional coatings. We have found that the most viscoelastic films occur at lower than ambient temperature when there is a monolayer of 2:1 aCD:surfactant inclusion complexes. Crucial data on the interfacial composition from neutron reflectometry (NR), as well as data from complementary bulk techniques, led to the formation of this physical picture. Now we aim to understand better the origin of the viscoelasticity, so we have recorded various lab data on systems with 3 different surfactant head groups. Also, we aim to control better the magnitude of the viscoelasticity, so we have worked on mixtures with different complexes. Yet in both cases we are missing data on the interfacial composition. So we apply for neutron beam time on FIGARO as only NR can resolve this information. Indeed for the mixtures we will use selective deuteration to resolve the interfacial stoichiometry of different inclusion complexes for the first time.

FIGARO Experimental Report: #9-10-1622

Performed by Beatrice Barletti, Yixuan Yan and Richard Campbell

Measurements were conducted on a newly reconfigured 4-position adsorption trough sample changer at 10 degrees C thanks to the careful preparation by Simon Wood. There were no technical problems related to condensation of water. The water bath was set at 0.3 degree C to achieve a liquid temperature in the trough of 10 degrees C. We should remember to acknowledge Simon in any resulting publication, and the deuterated surfactants were synthesised by James Tellam who we should credit as co-author.

40 samples were measured but 5 samples did not measure correctly: 4 samples because hC14TAB or dC14TAB was added in sufficient concentration to generate precipitate and bulk scattering that meant that there was no specular reflection to analyse, and 1 sample because it was misaligned so again there was no specular peak to analyse. 35 samples worked according to the following inventory and are named samples 1–35. The concentration of the added surfactant is stated as the amount in the final mixture (i.e. all stock solutions were three times this concentration).

Data for each sample were recorded for at least two hours. The main data plots are the data averaged over a timescale of 90–120 minutes after sample preparation. Kinetic plots of the data are available for review as well. Data are also available of the ‘last point’ that was recorded simply for reference, as this would be an arbitrary way to plot the data.

A problem was encountered in the experiment as hC14SO4 was not delivered on time, meaning that we we missed some data collection. To resolve the amounts of three components, we require measurements in 3 isotopic contrasts, although in the proposal we stated that we would ‘overdetermine’ the system by measuring the 4 contrasts to reduce experimental uncertainties.

As a result of having no hC14SO4, it was decided to ‘overdetermine’ two of the aCD/C8/C12 samples to check some combination of the validity of the approach, the ability of ourselves to make samples, and the ability of the samples both to equilibrate within 90 minutes and be impervious to isotope-specific effects. For one further aCD/C8/C12 sample we have three contrasts. However, for all seven aCD/C12/C14 samples, we have two contrasts, which we can use to resolve the amounts of both surfactants (with one important approximation) but not the amount of aCD. For the one C14TAB sample measured, we can get the amounts of aCD and C12SO4 but not C14TAB, so not very useful probably, and at least now we know that we cannot measure with neutrons at higher C14TAB concentrations as precipitation dominated the scattering leaving no specular signal to analyse.

As we are missing one contrast, we cannot resolve the amount of aCD, and I have used in the calculation of C14SO4 an approximation that the amount of aCD is constant at 1.27 μmol/m^2. The findings here are: the surface excess of C14SO4 greatly exceeds that of a surfactant monolayer, imply a multilayering structure, and there is a minimum in the surface excess of C14SO4 at the maximum value of the viscoelasticity. However, a limitation of the former finding is the approximation about the amount of aCD. A figure of reflectivity profiles can be provided in support.

On the basis of the above summary, a proposal was submitted to ISIS to complete this work. The proposal is copied on the next two pages and include more of the data analysis from the FIGARO experiment. One day of beam time was awarded on INTER, but due to issues with beam availability, the experiment took place on FIGARO instead, thanks to a gift of 1 day of easy access time, and it took place in June 2023. The experiment was successful, and its experimental objectives were completed.

Scientific Background

Aqueous solutions of α-cyclodextrin (αCD) and anionic surfactants, e.g. $Na^+C_xH_{2x+1}SO_4^-$ (C_xSO_4), spontaneously form highly viscoelastic films at the air/water interface [1]. The surface dilatational modulus, *E*, can be > 200 mN/m, and comparable values have been observed only for some protein systems under specific conditions [2]. During the last few years, we have investigated these systems extensively with aims of *understanding the origin* and *controlling the magnitude* of this remarkable behavior. Our motivation lies in the ambition to design films with specific chemical-mechanical properties that have interesting potential applications such as functional coatings ranging from medical diagnostics [3] to oil recovery [4].

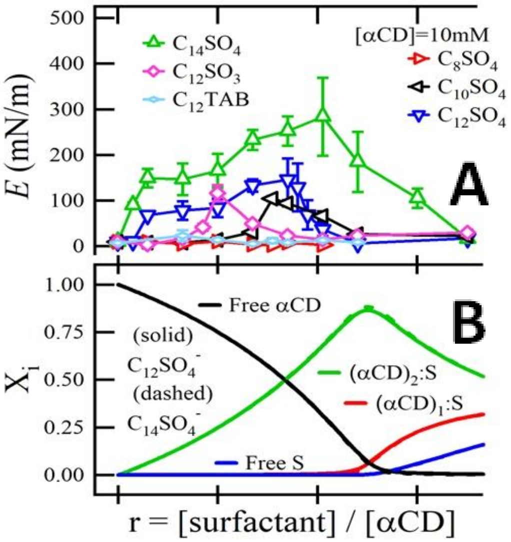

Fig. 1. (**A**) Surface dilatational modulus & (**B**) species distributions from isothermal titration calorimetry of 10 mM αCD/C_xSO_4 mixtures.

We have examined the viscoelasticity of these systems with measurements of *E* (where $|E| = d\gamma/d\ln A$, γ is the surface tension and *A* is the surface area) using a pendant drop for a range of surfactants including C_xSO_4 for x = 8/10/12/14 (Fig. 1A), and we have probed the bulk compositions (X_i) modelled from isothermal titration calorimetry data for x = 12/14 (Fig. 1B); data were recorded at 10 °C where the viscoelasticity is even higher than at room temperature.

A comparison of Figs 1A/B for x = 12/14 shows that high viscoelasticity occurs when the bulk solution is dominated by 2-αCD:1-C_xSO_4 inclusion complexes as well as free αCD, and the viscoelasticity is suppressed as the amount of 1:1 complexes or free surfactant increases. In our initial work, we hypothesised that the high viscoelasticity originates from the adsorption of 2:1 complexes, and the viscoelasticity for x = 8/10 is lower because the surfactant molecules are barely long enough to be encapsulated by two αCD molecules, but experimental validation of this hypothesis was needed.

Direct interfacial characterisation using neutron reflectometry

We went on to investigate the adsorption of αCD aggregates at the air/water interface [5], and the viscoelastic αCD/surfactant films for the x = 12 system [6], using neutron reflectometry (NR). In a plot of the interfacial composition with respect to the bulk stoichiometry, $r = [C_{12}SO_4]/[\alpha CD]$, using the low-Q analysis approach [7] (Fig. 2A), the first two data points in the viscoelastic region fit to a monolayer of 2:1 complexes with a residual amount of αCD aggregates. With increasing *r*, the surface excess of $C_{12}SO_4$ increases while that of αCD diminishes, and for *r* > 1 there is even more than a monolayer with a minimal amount of αCD, which we attribute to the Krafft point of the surfactant, i.e. when surfactant is released from the inclusion complexes it crystallizes at the interface and suppresses the viscoelasticity (Fig. 2B).

Structural data from NR show that the most viscoelastic sample of 10 mM αCD/3.4 mM $C_{12}SO_4$ fit to a single layer of 15 Å, i.e. close both dimensions of 2:1 complexes (Fig. 2C) [6], so it has not been possible to distinguish experimentally whether the complexes lie with the surfactant chains parallel or perpendicular to the surface. Indeed, there is controversy in the literature to this effect. Indications from MD simulations suggest that the driving force for adsorption is related to entropy gain from the release of water molecules around αCD, so the complexes lie with the chains parallel to the surface [8], whereas a recent study on film rheology shows agreement to data of a model with the driving force mediated by dipole-dipole interactions, so the complexes lie with the chains perpendicular to the surface [9]. Clearly more work is required to distinguish these possibilities.

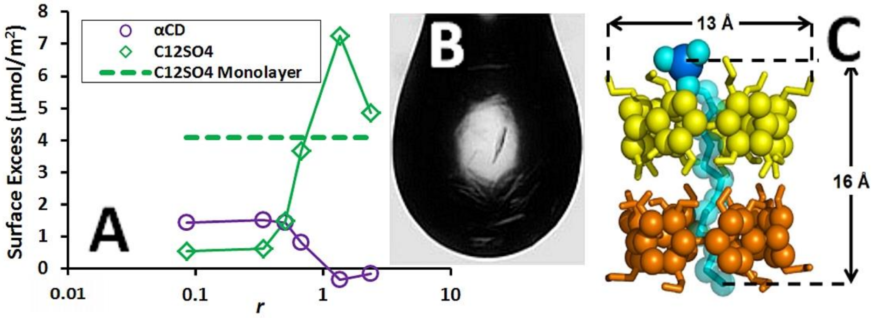

Fig. 2. (**A**) NR interfacial composition of 10 mM αCD/$C_{12}SO_4$ mixtures. (**B**) Photo of a droplet with the highest surface excess of $C_{12}SO_4$. (**C**) 2:1 complex snapshot.

New work on αCD/mixed surfactant systems

Recently, we turned our attention to αCD/mixed surfactant systems by measuring *E* of 10 mM αCD/3.4 mM $C_{12}SO_4$/C_xSO_4 mixtures for x = 8 and 14 (Fig. 3A). While addition of C_8SO_4 reduces the viscoelasticity, addition of $C_{14}SO_4$ increases it further. It could be that the magnitude of the viscoelasticity is related to the least favourable conditions for αCD aggregates to adsorb and hence the coverage of 2:1 complexes is highest. However, without direct interfacial characterization, this hypothesis remains only a guess.

We were supported to resolve the interfacial composition of the αCD/$C_{12}SO_4$/$C_{14}SO_4$ system in 2 days on the FIGARO reflectometer in September 2021 (#9-10-1622) in a collaboration with the ISIS Deuteration Facility who provided the deuterated surfactants. This technically challenging experiment at 10 °C was possible thanks to the development of a 4-position insulated adsorption trough assembly with water bath circulation, heater wires and condensed air flow to prevent condensation on the windows (Fig. 3B). Using the low-Q analysis approach [7], measurements of samples in 3 combinations of isotopic contrasts of the interfacial material, all in null reflecting water (NRW), would have been sufficient to resolve the surface excesses of αCD, $C_{12}SO_4$ and $C_{14}SO_4$. However, in spite of h-$C_{14}SO_4$ being ordered in plenty of time, and it being stated for delivery in time, upon our arrival at the ILL it emerged that the delivery had been put back to November 2021. The experiment went ahead but only two contrasts per sample could be measured, which are insufficient to resolve the surface excesses of the three interfacial components. Preliminary analysis of the data has been possible only using a crude assumption of a fixed αCD surface excess (Fig. 3C). The αCD surface excess, and hence the complex stoichiometry, remain missing, and the unvalidated assumption made could mask large errors, which means that without collection of the missing data, our results are not publishable. Even so, there appears to be a minimum in the $C_{14}SO_4$ surface excess coinciding with the highest viscoelasticity (red dashed line in Fig. 3C), and the $C_{14}SO_4$ surface excess greatly exceeds that of a monolayer hinting at a fundamentally different structure responsible for the high viscoelasticity.

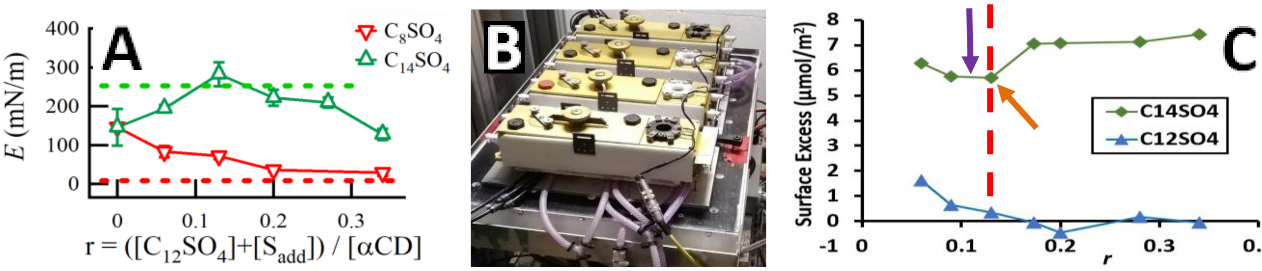

Fig. 3. (**A**) Surface dilatational modulus of 10 mM αCD/3.4 mM $C_{12}SO_4$/C_8SO_4 (red) and 10 mM αCD/3.4 mM $C_{12}SO_4$/$C_{14}SO_4$ (green) mixtures; dashed lines = reference C_8SO_4 and $C_{14}SO_4$ values. (**B**) Photo of the experimental setup developed on FIGARO to conduct the work. (**C**) Equivalent data to that in panel A of interfacial compositions from NR.

Equipment, samples, request & outlook

We request _1 day on INTER_ to complete this work. In true collaboration, the ILL agrees that the 4-trough cooling assembly can be sent to ISIS; costs will be covered by the PI if the ISIS consumables fund cannot be used. As such, we will be able to record sets of 4 samples, which we have shown take 4 h each. The 16 samples are: (1) the missing αCD/h-$C_{12}SO_4$/h-$C_{14}SO_4$/NRW contrast for the 7 compositions shown in Fig. 3C, (2) 3 new contrasts at 1.05 mM [$C_{14}SO_4$] in NRW around the $C_{14}SO_4$ surface excess minimum (purple arrow), (3) 3 repeat contrasts at 1.20 mM [$C_{14}SO_4$] in NRW at the viscoelasticity maximum (orange arrow), (4) 2 extra contrasts with h- and d-surfactants at 1.20 mM [$C_{14}SO_4$] in D_2O to reveal the interfacial structure, and (5) 1 more repeat sample. We allow 8 h for setup and temperature/beam/solvent calibrations. We have in our possession αCD and all the surfactants we need already. This short experiment will deliver novel insight into the interfacial composition _and_ structure of the high viscoelasticity for an αCD/mixed surfactant system for the first time and allow our NR data to be incorporated in an immediate publication.

References.

[1] J. Hernandez-Pascacio et al. *J. Phys. Chem. B* **2007**, *111*, 12625; [2] D. J. Burgess et al. *J. Colloid Interf. Sci.* **1997**, *189*, 74; [3] V. N. Kazakov et al. Ch 13 in Interfacial Rheology. Progress in Colloid and Interface Science. Eds R. Miller and L. Liggieri, 2009, Brill, Leiden-Boston; [4] H-Q. Sun et al. *Soft Matter* **2011**, *7*, 7601; [5] J. Hernandez-Pascacio et al. *Langmuir* **2016**, *32*, 6682; [6] A. S. Luviano et al. *J. Colloid Interf. Sci.* **2020**, *565*, 601; [7] L. Braun et al. *Adv. Colloid Interf. Sci.* **2017**, *147*, 230; [8] P. Brocos et al. *J. Phys. Chem. B* **2010**, *114*, 12455; [9] J. R. Romero-Arias et al. *Soft Matter* **2021**, *17*, 2652.