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The bulk and surface properties of aqueous α -cyclodextrins (α -CD) / surfactant mixtures have been extensively studied with a variety of techniques. In this work, α -CD and anionic surfactants (n-alkyl sulfates ($C_nSO_4^-$) with $n = 8$ to 14, and the sulfonate $C_{12}SO_3^-$) were found to spontaneously form viscoelastic films at aqueous solution/air interfaces. Temperature, concentration, alkyl chain length and the number of surfactants employed strongly modify their viscoelastic properties.



Figure 1. Snapshots of a video showing the remarkable viscoelastic behavior of a film at the solution/air interface of {4.1 mM $C_{12}SO_4^-$ + 10 mM α -CD + water} ($r = 0.41$) at 283 K during drop volume reduction. Notice that there is no neck reduction.

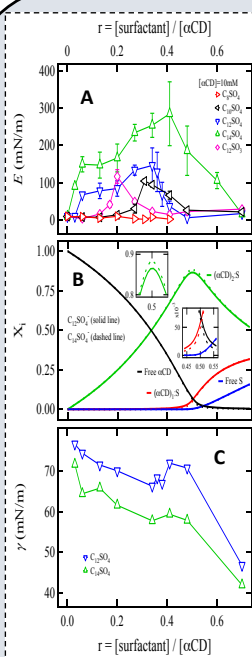


Figure 2.1. (A) Dilatational modulus (E) for five anionic surfactants at 283 K as a function of the concentration ratio $r = [\text{surfactant}]/[\alpha\text{-CD}]$. In these experiments, the concentration of α -CD was kept constant and equal to 10 mM and the frequency of the sinusoidal periodic oscillation was 0.2 Hz.

The only common species which links the high viscoelasticity for all the systems and r values is the presence of 2:1 complexes in the bulk.

(B) Distribution of species at 283 K in the bulk solution for $C_{12}SO_3^-$ and $C_{12}SO_4^-$ at 283 K obtained from ITC.

(C) Surface tension for $C_{12}SO_3^-$ and $C_{12}SO_4^-$ at 283 K.

Figure 2.2 (D) Dilatational modulus (E) for $C_{12}SO_3^-$ at 283 K and 293 K as a function of α -CD concentration keeping $r = [\text{surfactant}]/[\alpha\text{-CD}]$ constant and equal to 0.34. In these experiments, the sinusoidal periodic oscillation was 0.2 Hz. The error bars are the standard deviations obtained from the measurements of three different drops.

(E) Distribution of species in the bulk solution at 283 K and 293 K for $\{C_{12}SO_3^- + 10 \text{ mM } \alpha\text{-CD}\}$ calculated with AFFINmeter [REF 1] with K_{11} and K_{21} from Table 1.

(F) Corresponding surface tension values where the most dilute solution corresponds to 1 mM α -CD.

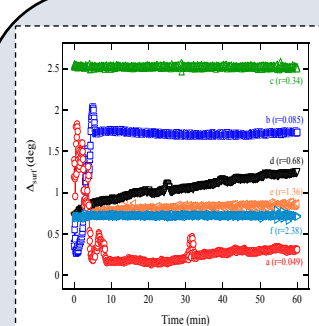
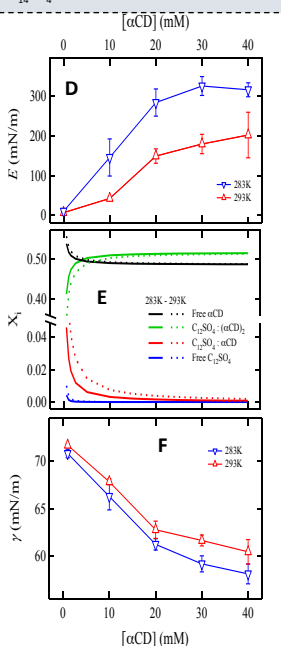


Figure 3.1. Kinetic evolution of the ellipsometry phase shift (Δ_{surf}) for the $\{C_{12}SO_4^- + 10 \text{ mM } \alpha\text{-CD}\}$ system at 283 K for six different concentration ratio $r = [\text{surfactant}]/[\alpha\text{-CD}]$

At low r (where α -CD is the majority material in the bulk), we observe a slow kinetic adsorption at the surface with temporal fluctuations in Δ_{surf} that indicate the formation of an inhomogeneous layer, which correlates clearly to what has been observed for the adsorption of α -CD aggregates [REF 2]

As we increase r , the adsorption kinetics are faster and the fluctuations are reduced or disappear due to surface competitive adsorption of 2:1 complexes giving as a result a more homogenous and ordered layer. Beyond this $r=0.34$, the presence of the incremental free surfactant dominates the adsorption at the surface.

Table 1. Values for the distribution of species at 283 K in the bulk solution (%) for the $\{C_{12}SO_3^- + 10 \text{ mM } \alpha\text{-CD}\}$ system for several r values obtained from ITC measurements.

	$r = [C_{12}SO_3^-]/[\alpha\text{-CD}]$					
	a	b	c	d	e	f
2:1 complexes (%)	5.2	9.3	50.9	58.3	20.0	8.1
1:1 complexes (%)	0.01	0.02	0.32	29.17	33.6	25.6
Free surfactant (%)			0.00	11.9	46.2	66.2
Free α -CD (%)	94.7	90.6	48.8	0.59	0.09	0.02

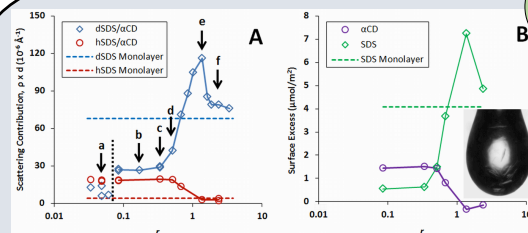


Figure 4.1. (A) Scattering contributions in the low- q analysis method of NR for the $\{C_{12}SO_4^- + 10 \text{ mM } \alpha\text{-CD}\}$ system at 283 K for different concentration ratios $r = [\text{surfactant}]/[\alpha\text{-CD}]$, where labels a-f correspond to the same samples measured using ellipsometry; red and blue horizontal dashed lines mark the respective scattering contributions for a full monolayer of $h\text{-}C_{12}SO_4^-$ and $d\text{-}C_{12}SO_4^-$ **(B)** Resulting surface excesses from analysis of the data in panel A using the methodology described in REF 3; horizontal dashed line marks the value for a full SDS monolayer. The inset is a photograph of a hanging droplet of sample e where micro-crystals at the water/air interface can be observed.

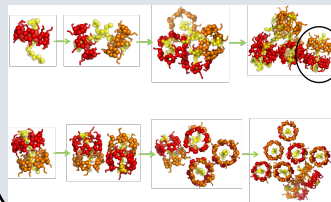


Figure 4.2. MD simulation snapshots after 50 ns show the aggregation pattern for both types of complexes: antiparallel cylinders for the 2:1 complexes and $C_{12}SO_4^-$ tail-driven aggregates for 1:1 complexes.

Conclusion

It was found that the viscoelastic behavior is strongly related to the distribution of species in the bulk solution, in particular to the high concentration of α -CD₂-surfactant inclusion complexes, but also to their relative surface activity.

References

- REF 1. Angel Piñeiro et al., AFFINmeter: A software to analyze molecular recognition processes from experimental data, Analytical Biochemistry, 2019, in press.
REF 2. Jorge Hernandez-Pascacio, Angel Piñeiro, et al. Complex Behavior of Aqueous α -Cyclodextrin Solutions. Interfacial Morphologies Resulting from Bulk Aggregation. Langmuir, 2016, 32,6682-6690. DOI:10.1021/acs.langmuir.6b01646.
REF 3. Braun, L.; Uhlig, M.; von Klitzing, R.; Campbell, R. A. Polymers and Surfactant at Fluid Interfaces studied with Specular Neutron Reflectometry. Adv. Colloid Interface Sci. 2017, 247, 130-148.