



Interactions between polymeric surfactants and bile salts: new routes for controlling lipid digestion of oil-in-water emulsions

Amelia Torcello Gómez¹
Julia Maldonado Valderrama²
Ana B. Jódar Reyes²
Timothy J. Foster¹

Outline

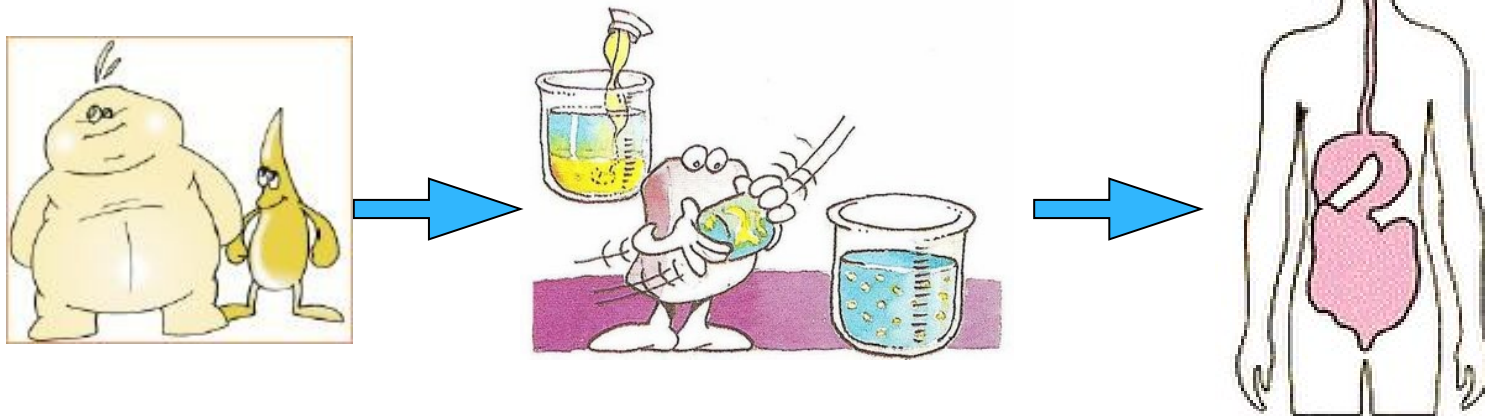
- Introduction and Aims
- Experimental Section
- Results and Discussion:
 - Interactions in aqueous phase
 - Interactions at the oil-water interface
 - Interactions in Pluronic-stabilised emulsions
- Conclusions
- Acknowledgements



Introduction

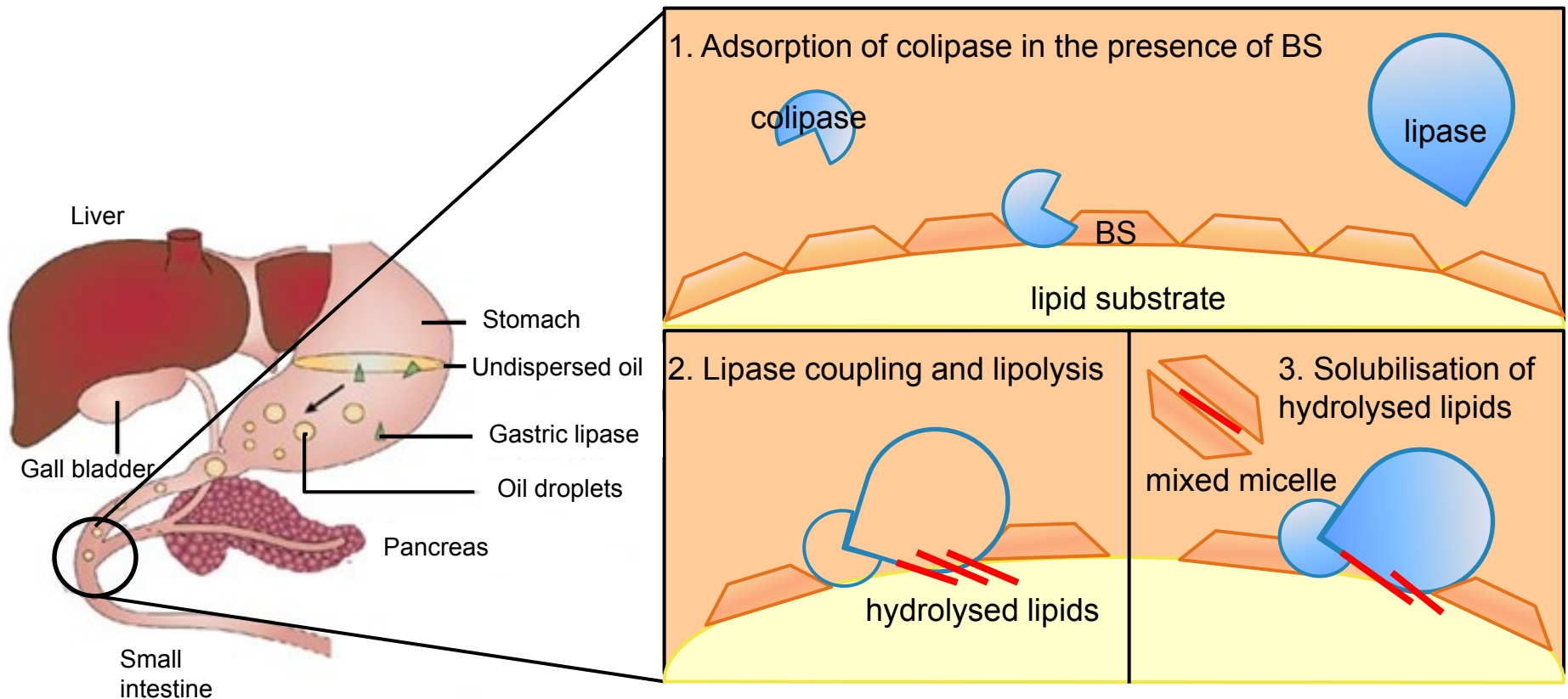


- Controlling lipid digestion profiles would facilitate the development of remodeled lipids with tailored properties:
 - Control of satiety
 - Delivery of bioactive components to specific locations
- Lipids are present as O/W emulsions



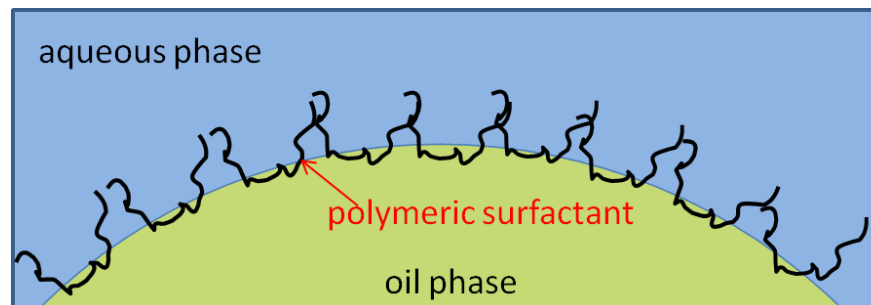
Introduction

- Bile salts (BS) replace original emulsifier from the surface of lipid droplets preparing the interface for lipolysis



Introduction

- Bile salts (BS) replace original emulsifier from the surface of lipid droplets preparing the interface for lipolysis
- Lipolysis is an **interfacial** reaction that can be affected
 - by the presence of emulsifiers onto the oil-water interface:
 - either more surface active than BS
 - and/or resistant to displacement by BS
 - by **events** taking place in the **bulk** that may have an impact on the interfacial properties



Background

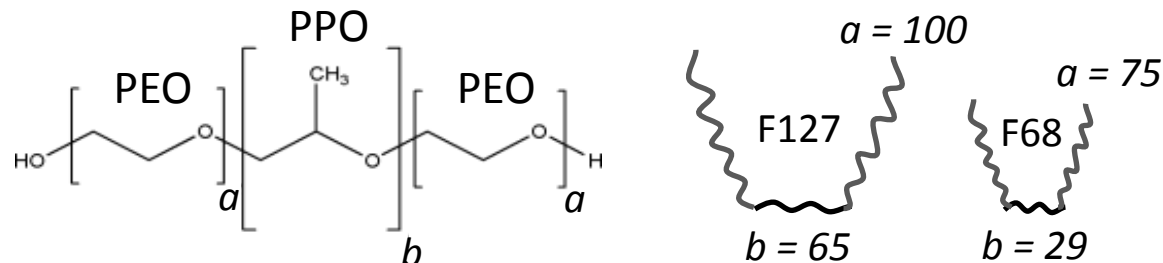
- Pluronic surfactants opening up new horizons in the control of lipid digestion (approved for oral intake by U.S. FDA)
- **Delay lipid digestion** as compared with model emulsifiers (lecithin or proteins)

📖 M. Wulff-Pérez, M.J. Gálvez-Ruiz, J. de Vicente, A. Martín-Rodríguez, Food Res. Int. 43 (2010) 1629.

📖 A. Torcello-Gómez, J. Maldonado-Valderrama, A. Martín-Rodríguez, D.J. McClements, Soft Matter 7 (2011) 6167.

- Adsorbed layers provide a **steric barrier** which protects the o-w interface from the action of BS and lipase
- Oil droplets covered by larger Pluronic (F127) are digested at lower rate and extent than those covered by smaller Pluronic (F68)

📖 M. Wulff-Pérez, J. de Vicente, A. Martín-Rodríguez, M.J. Gálvez-Ruiz, Int. J. Pharm. 423 (2012) 161.



Aims

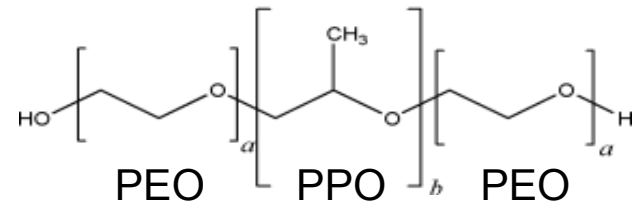


- Analyse the **bulk interactions** between Pluronics (F127 or F68) and a bile salt (NaTDC) in Pluronic-stabilised emulsions
 - Evaluate the **impact of these interactions** on the **o-w interface** in emulsions
 - Study in aqueous phase
 - Study at oil-water interface
 - Effect of the molecular differences of both Pluronics
- Deepen the understanding of the mechanisms underlying lipid digestion of Pluronic-stabilised emulsions

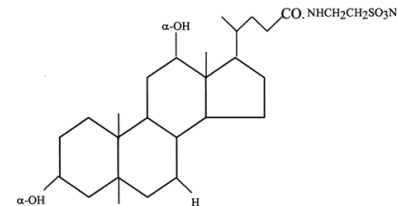
Experimental Section: Materials

- Pluronics: non-ionic triblock copolymers

- **F68**: MW=8400 g/mol, 16% PPO
- **F127**: MW=12600 g/mol, 25% PPO



- Bile salt: **NaTDC**, MW=521.7 g/mol



- Aqueous phase: 1.13 mM phosphate buffer, pH 7

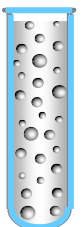
- Oil phase: highly refined and purified **Olive Oil**

- $\gamma_0 = 29.5$ mN/m, $T = 20$ °C
- (density: 0.91 g/cm³, mean MW 800 g/mol)



- **Emulsion** preparation: ULTRA-TURRAX[®] homogenizer (IKA[®] T18 basic)

- 10 wt% oil phase
- 90 wt% F68 or F127 aqueous phase at 1 wt%



Experimental Section: Micro-DSC



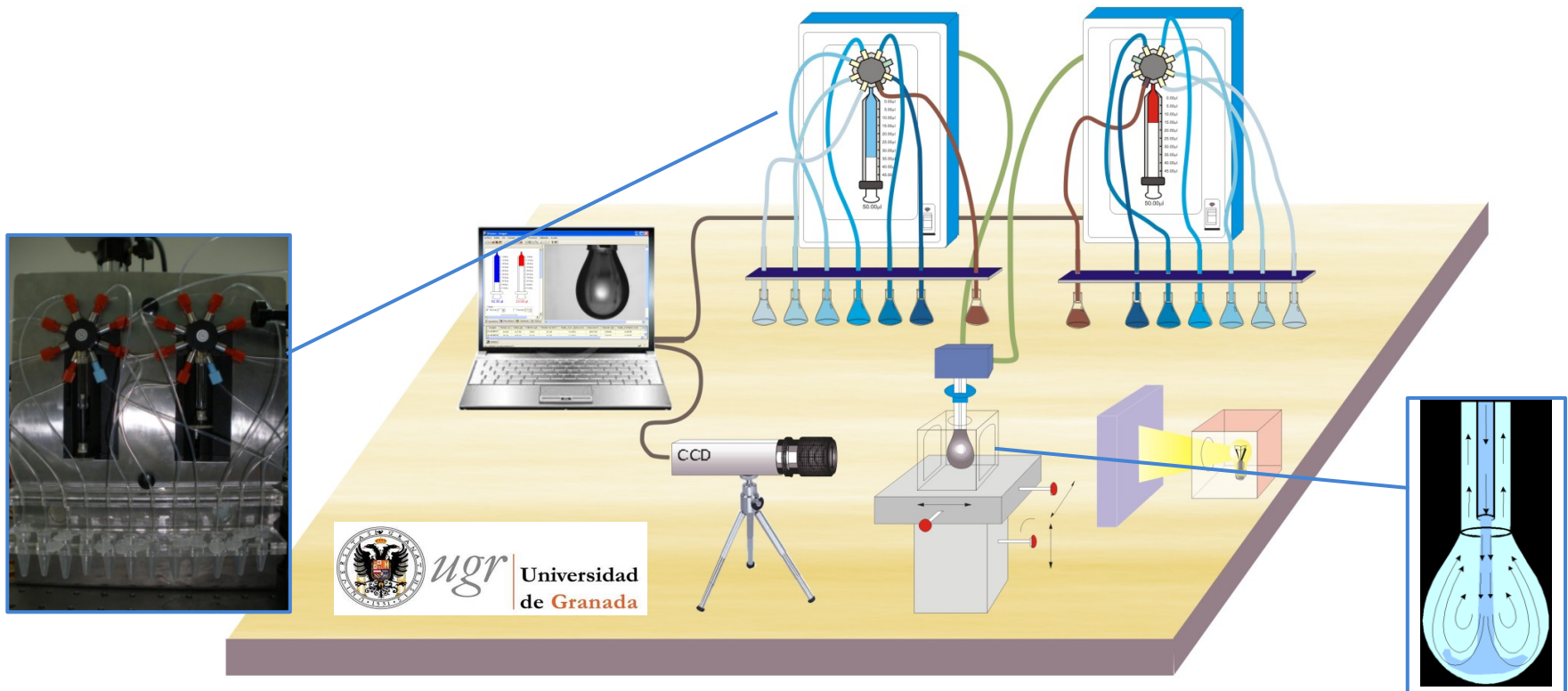
- Micro-Differential Scanning Calorimetry: DSC III Setaram
- Sample weight: 800 mg
- Scanning rate: 1 °C/min
- Heating/cooling cycles: 10-90 °C
- Interactions between Pluronic and NaTDC in aqueous phase and in Pluronic-stabilised emulsions



Experimental Section: The Octopus



- Pendant Drop Surface Film Balance equipped with **subphase multi-exchange** device



Octopus Software-Dinaten© Dr. Juan Antonio Holgado-Terriza

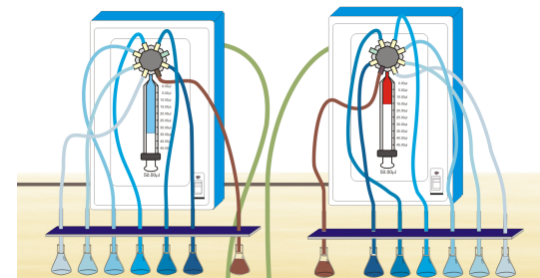
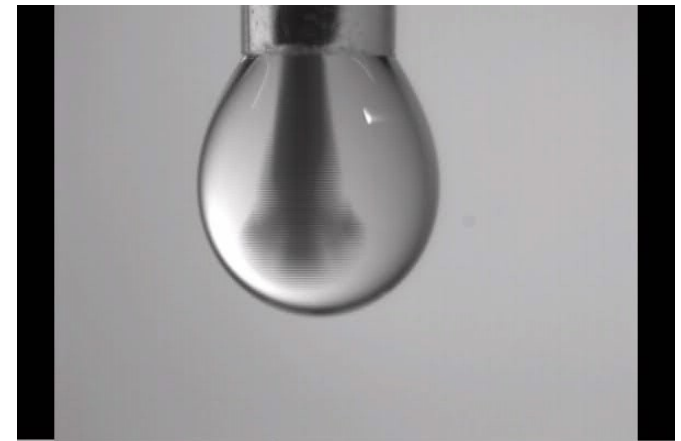
Cabrerizo-Vílchez et al. Patent *submitted* (P201001588)

Experimental Section: The Octopus


■ Operation

■ Double capillary

- Normal capillary is substituted by an arrangement of **two coaxial capillaries**
- **Connected to both syringes** by channels of the 8 port-valve micro-injectors
- Both **syringes** operate **independently**
- **Automatic, non-invasive** and **complete exchange** of the subphase of the drop with different solutions
- Pendant drop volume and interfacial area are preserved during the subphase exchange

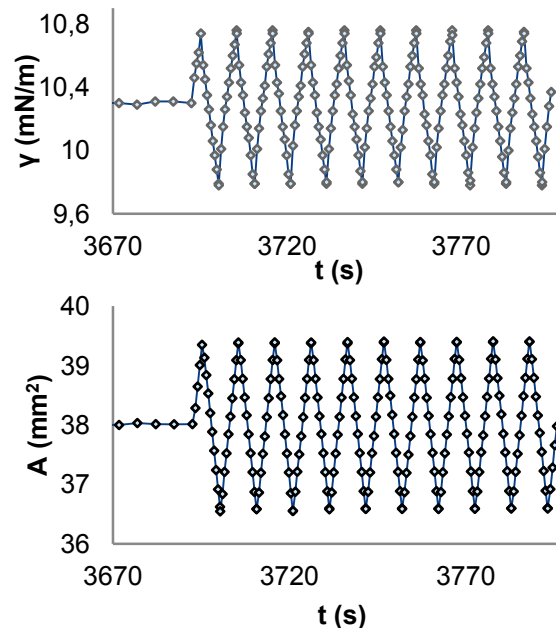
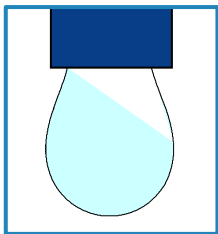


 Cabrerizo-Vilchez et al. Spanish Patent, registration number: P9801626.

 Ferri, Kotsmar and Miller. From surfactant adsorption kinetics to asymmetric nanomembrane mechanics: Pendant drop experiments with subphase exchange. *Adv. Colloid Interface Sci.*, 2010.

Experimental Section: The Octopus

- Operation
 - Interfacial dilatational rheology
 - Small-amplitude < 10 % (Viscoelastic Linear Regime)
 - $f = 0.1$ Hz



$$E = \frac{d\gamma}{d \ln A}$$

$$E^* = E' + iE'' = \varepsilon + i2\pi f\eta$$

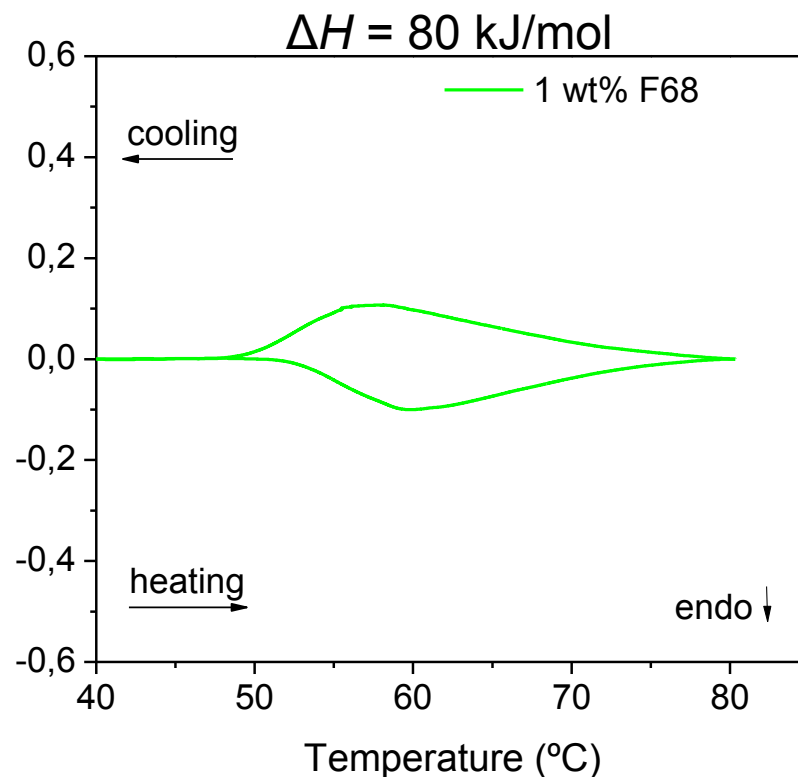
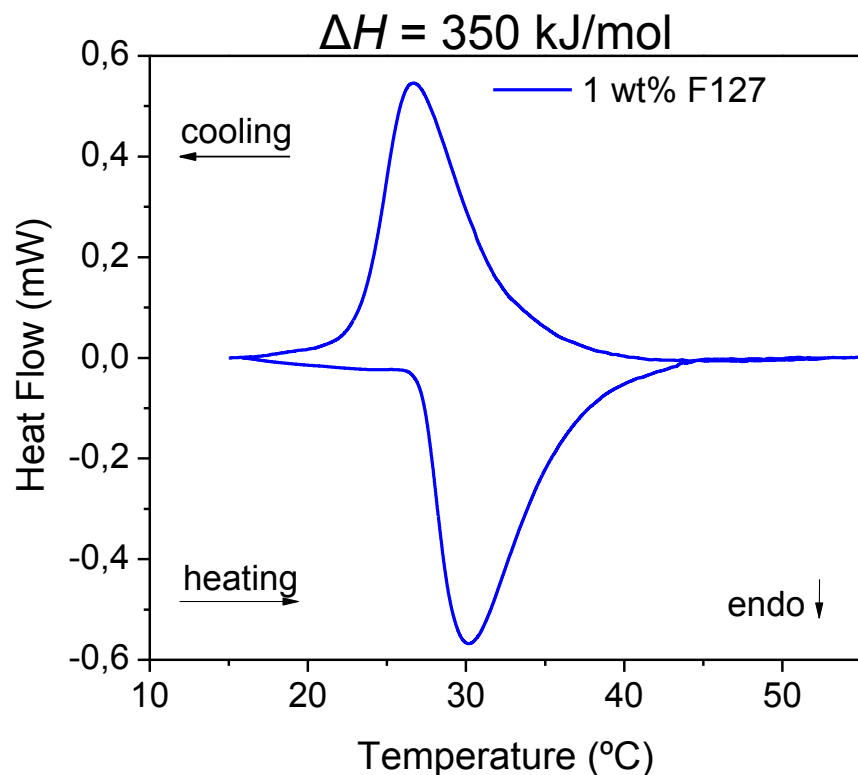
Experimental Section: The Octopus



- Interactions at the o-w interface:
 - Sequential adsorption of Pluronics and NaTDC
 - Competitive adsorption of Pluronics and NaTDC
- Record *in-situ* the **interfacial tension** during the whole process of adsorption
- Measure the **dilatational elastic modulus** at the end of each step of adsorption

Results: Interactions in aqueous phase

■ Micro-DSC



E. Hecht, H. Hoffmann, *Langmuir*, 10 (1994) 86.

P. Alexandridis, T. Nivaggioli, T.A. Hatton, *Langmuir*, 11 (1995) 1468.

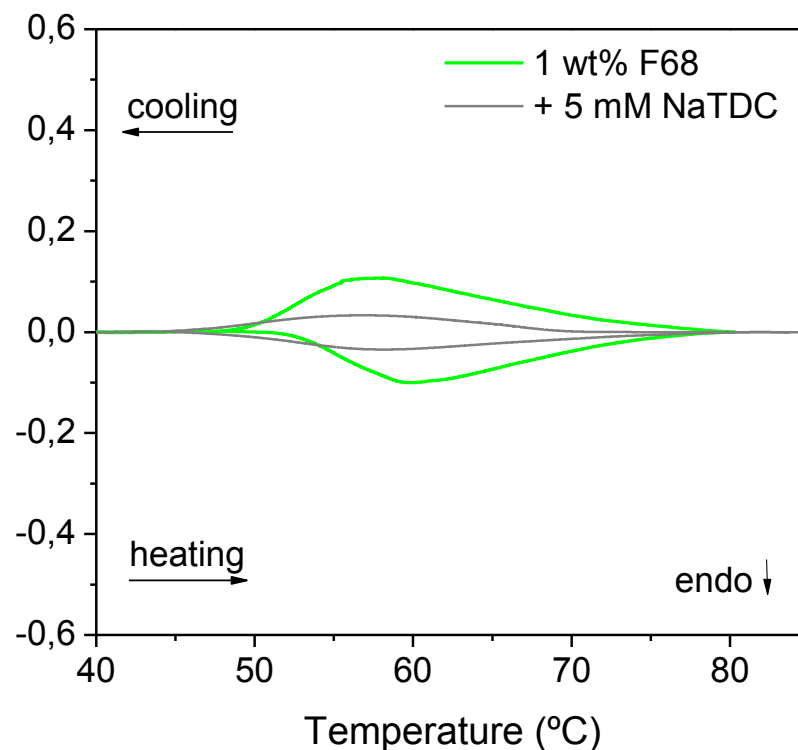
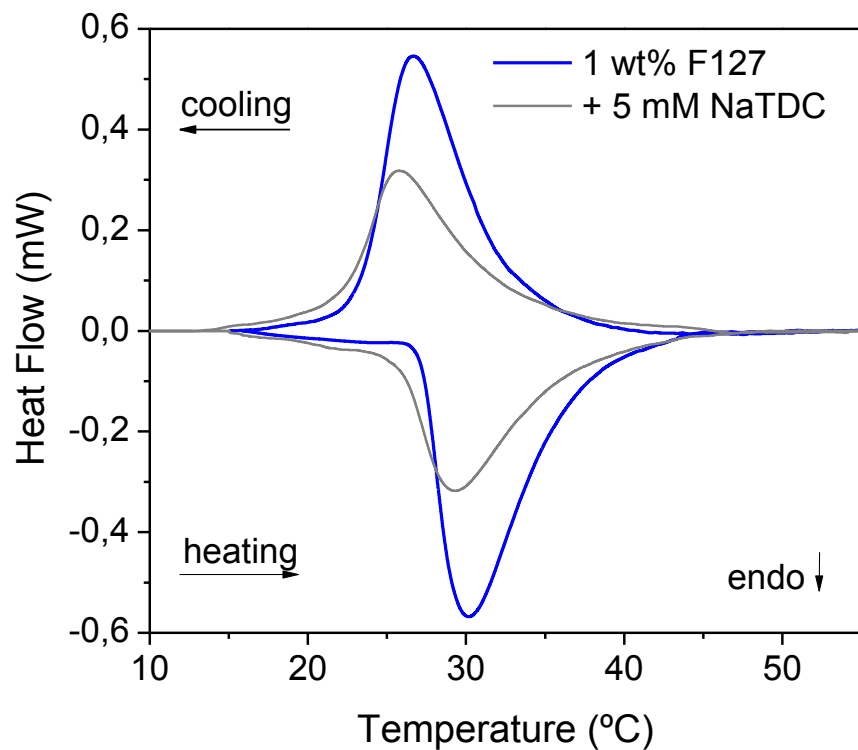
A. Cabana, A. Ait-Kadi, J. Juhász, *J. Colloid Interface Sci.*, 190 (1997) 307.

A.A. Barba et al., *J. Applied Polymer Sci.*, 114 (2009) 688.

I. Boucenna et al., *Langmuir*, 26 (2010) 14430.

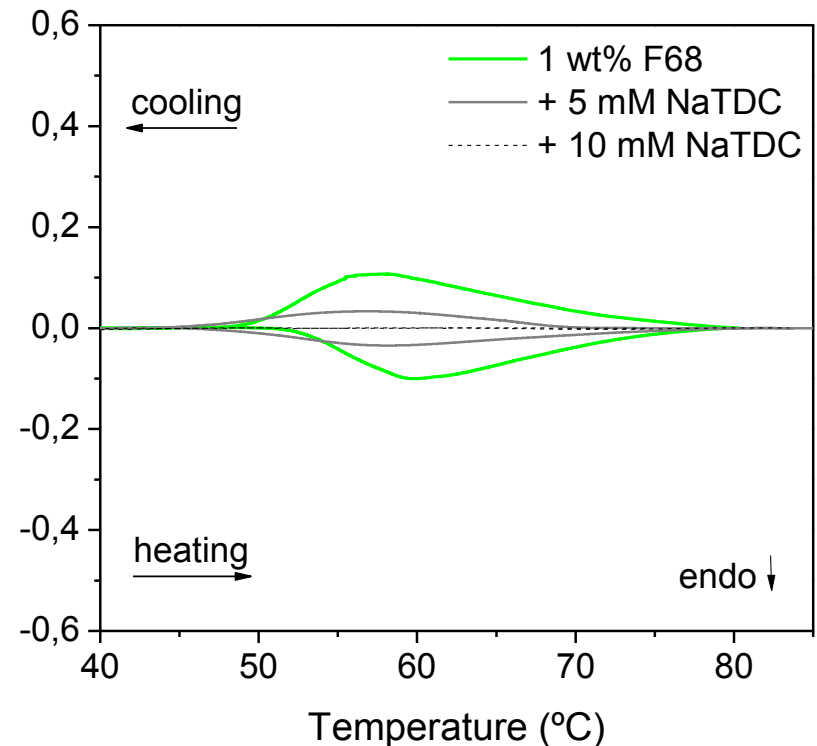
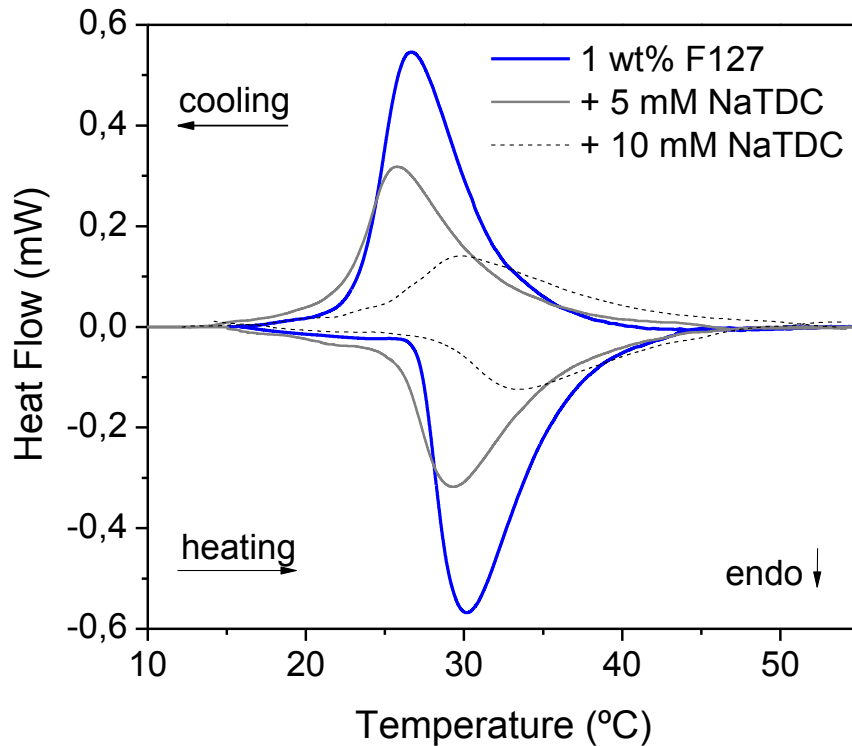
Results: Interactions in aqueous phase

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Results: Interactions in aqueous phase

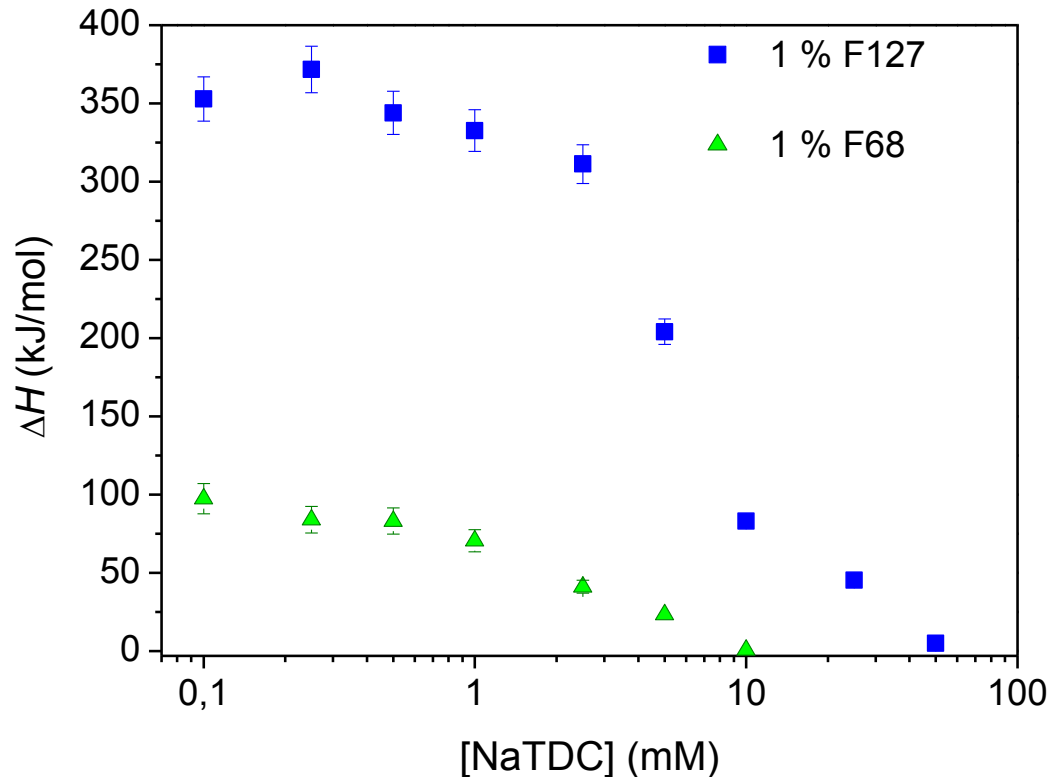
■ Micro-DSC



- Lower NaTDC concentration seems to suppress micellization of Pluronic F68

Results: Interactions in aqueous phase

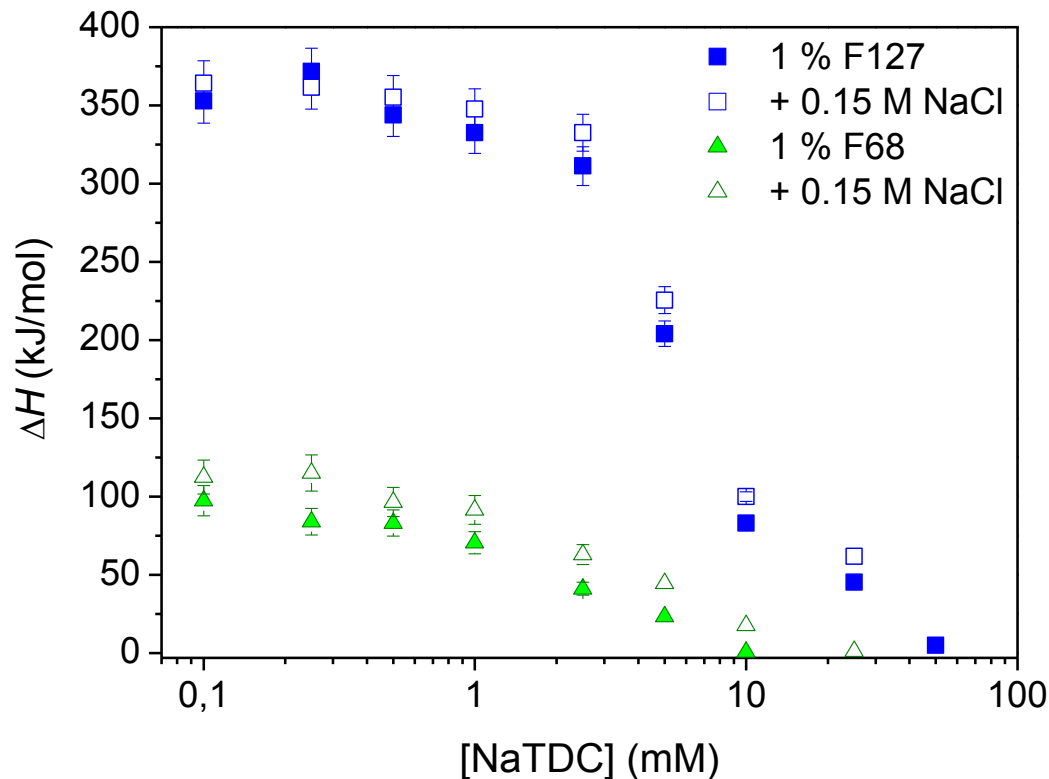
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- Lower NaTDC concentration seems to suppress micellization of Pluronic F68
- F127 interacts with larger amount of NaTDC molecules

Results: Interactions in aqueous phase

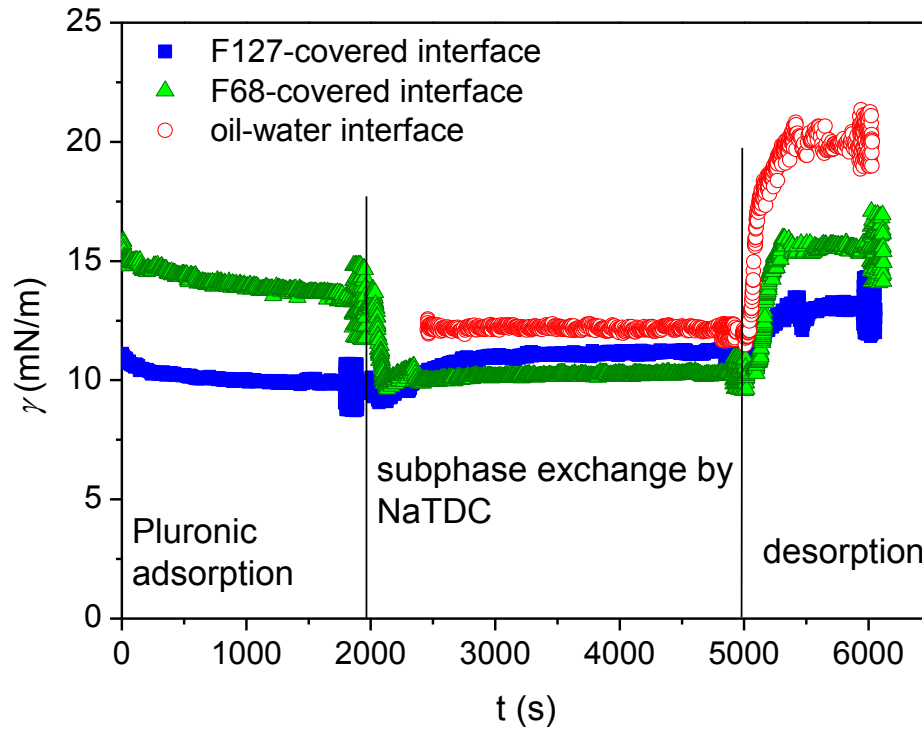
■ Micro-DSC



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- F127 interacts with larger amount of NaTDC molecules
- NaCl allows more compact arrangement of BS within mixed complexes

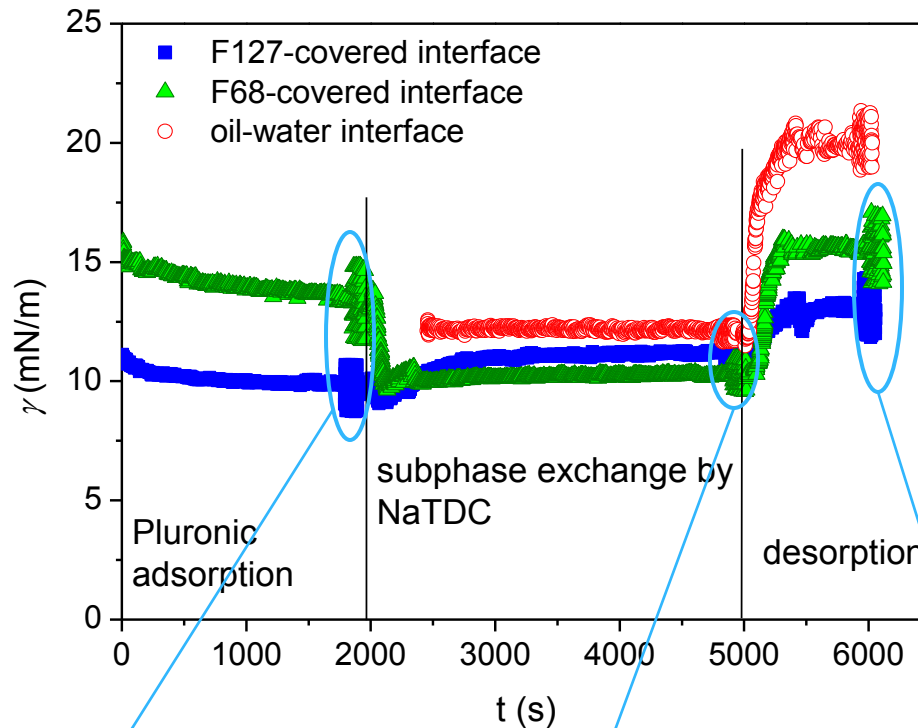
Results: Interactions at the o-w interface

- Sequential adsorption of NaTDC and desorption



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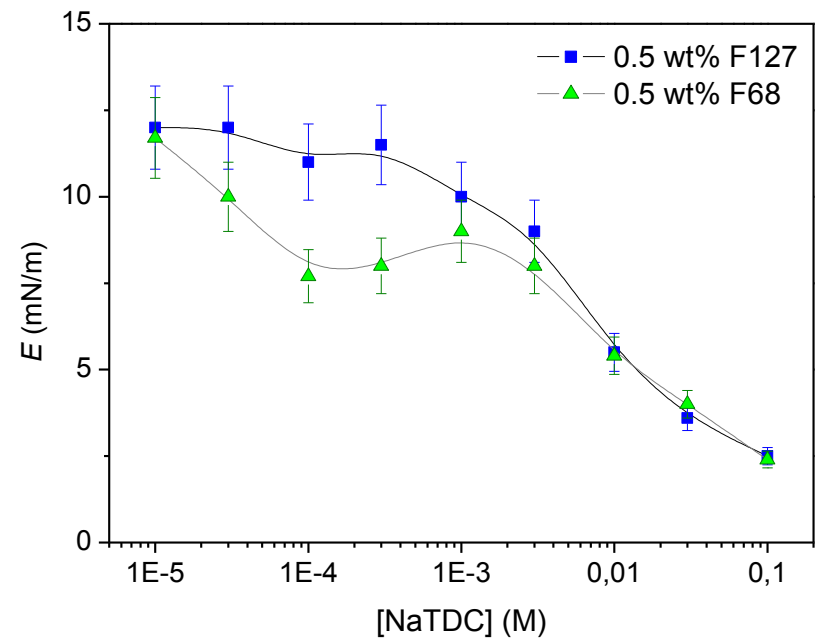
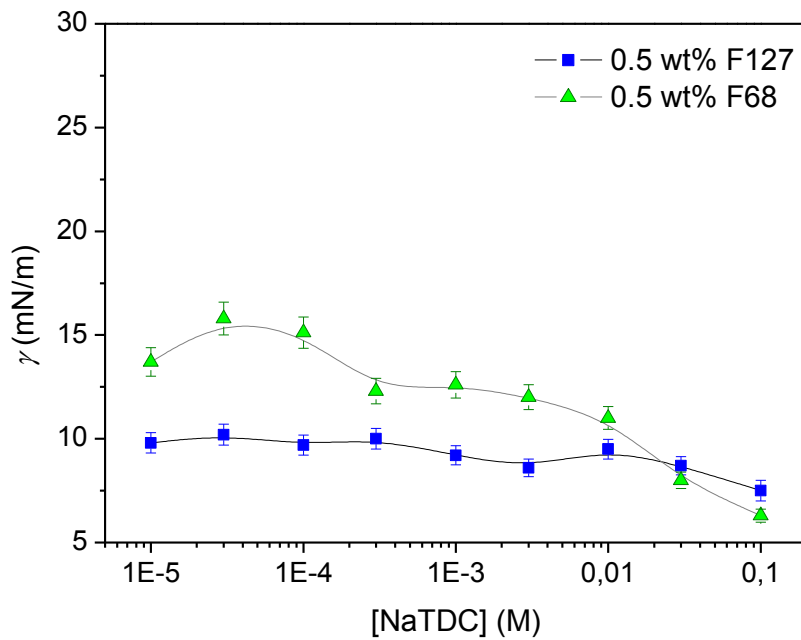


- F68 is more susceptible to be displaced by NaTDC

STEPS	1 wt% Pluronic adsorption		10 mM NaTDC adsorption		Desorption		
	Pluronic	γ (mN/m)	E (mN/m)	γ (mN/m)	E (mN/m)	γ (mN/m)	E (mN/m)
F68		13.0 ± 0.5	12 ± 1	10.0 ± 0.5	5 ± 1	15.0 ± 0.5	14 ± 1
F127		10.0 ± 0.5	12 ± 1	11.0 ± 0.5	6 ± 1	13.0 ± 0.5	14 ± 1

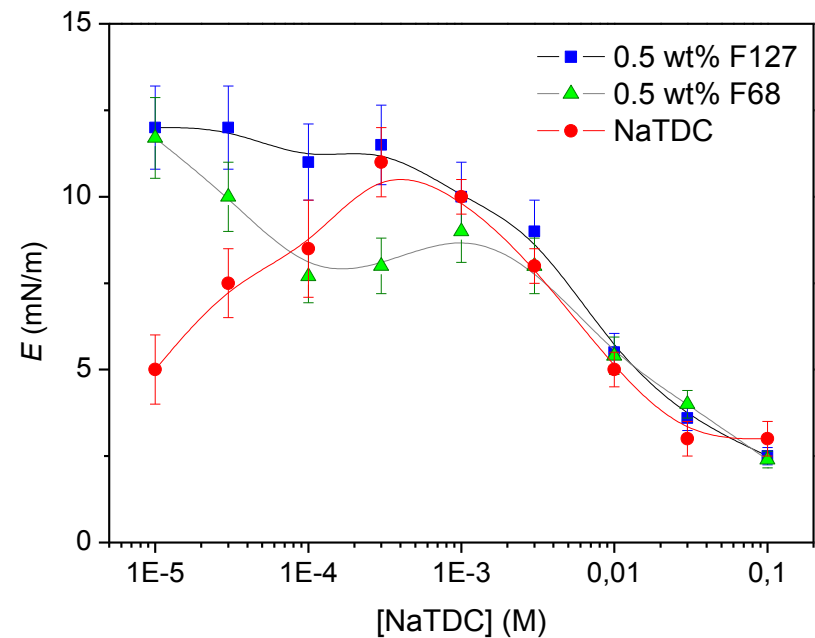
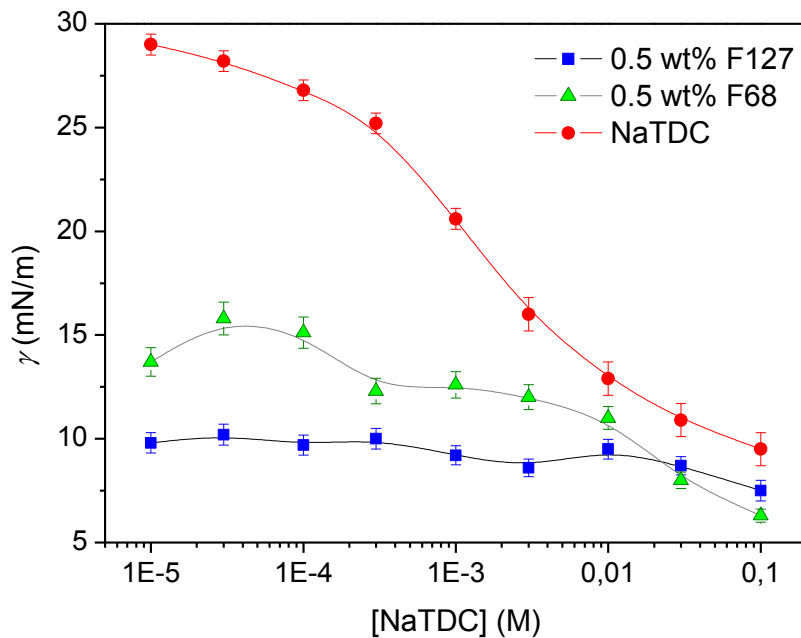
Results: Interactions at the o-w interface

■ Competitive adsorption with NaTDC (1h)



Results: Interactions at the o-w interface

Competitive adsorption with NaTDC (1h)

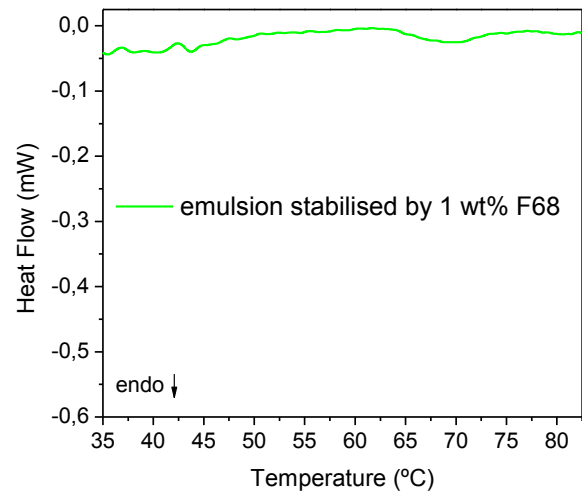
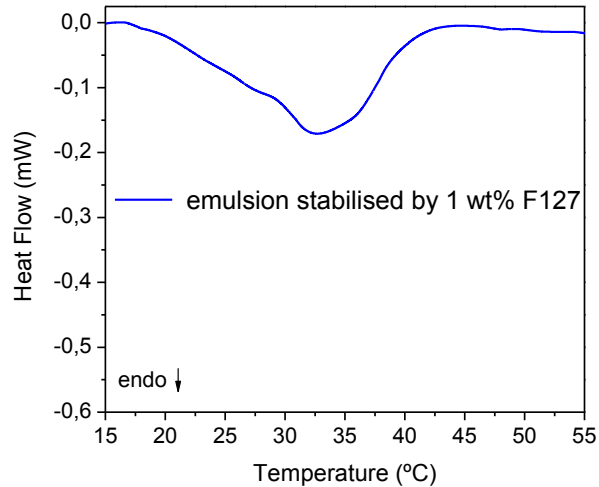


- Pluronic compete with bile salts for the oil-water interface
- F127 better competes for the oil-water interface with NaTDC

Results: Interactions in Pluronic-stabilised emulsions



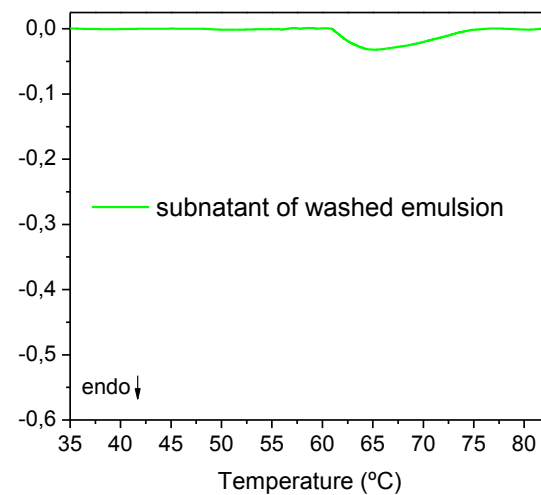
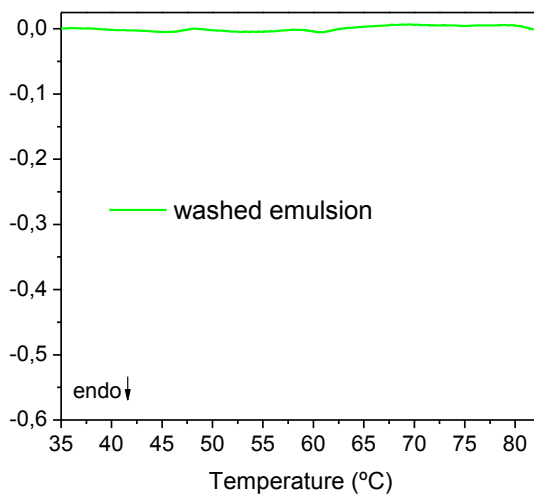
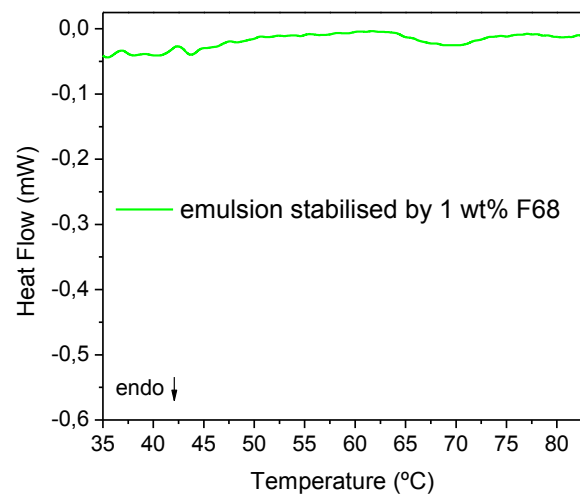
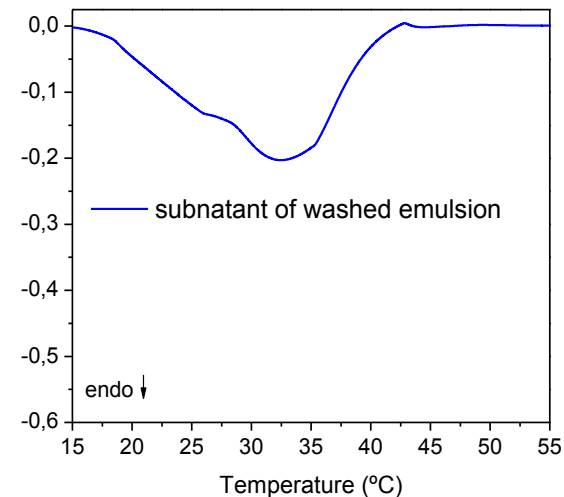
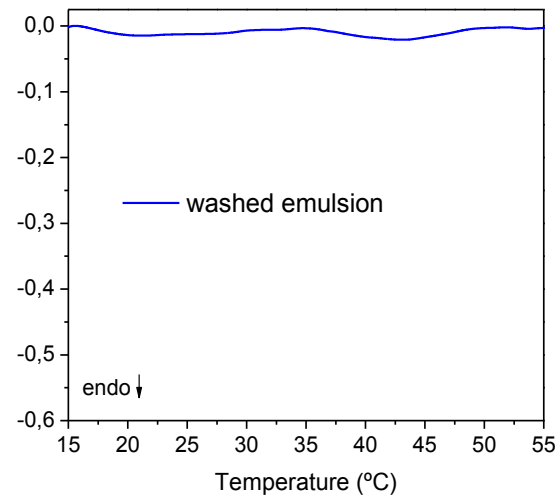
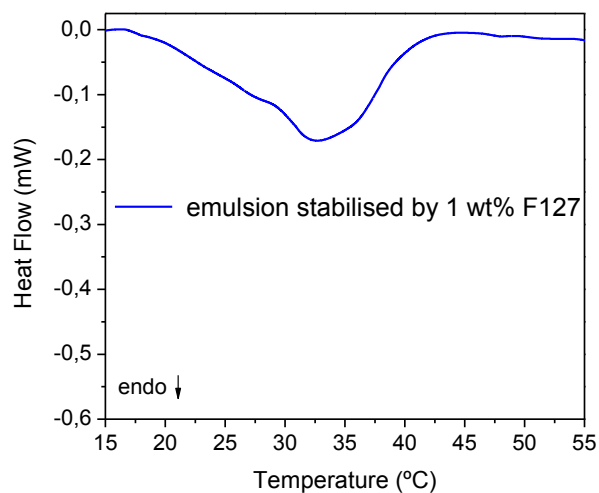
■ Micro-DSC



Results: Interactions in Pluronic-stabilised emulsions



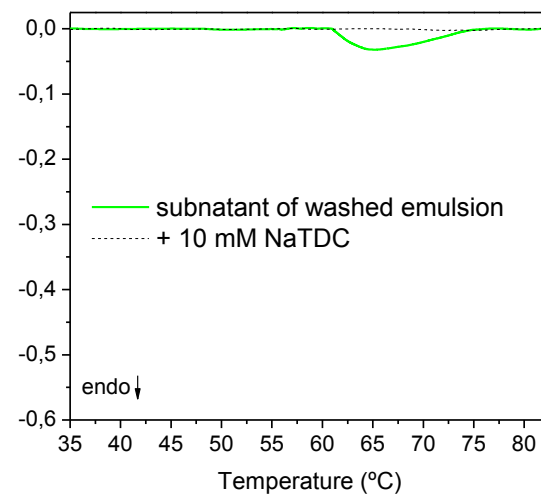
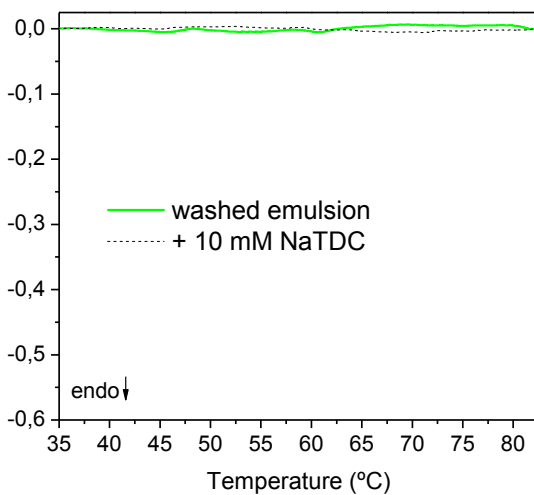
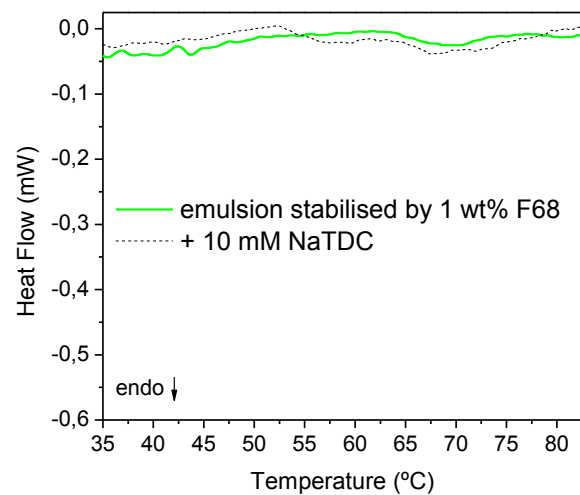
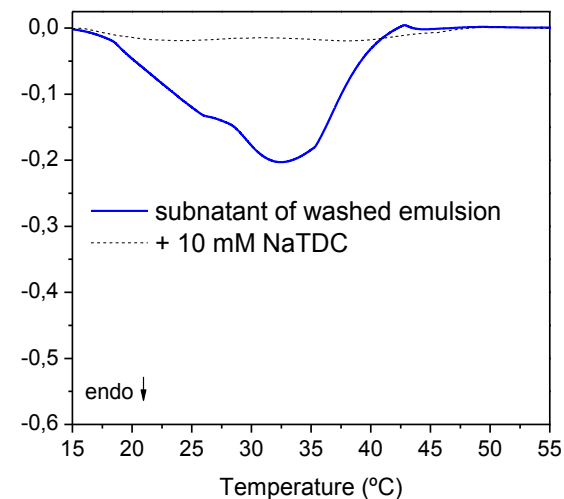
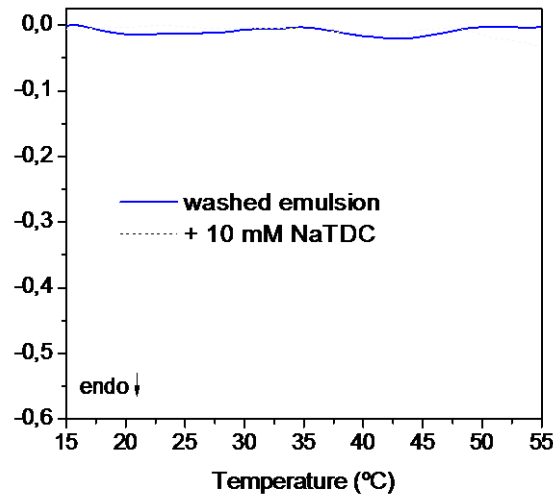
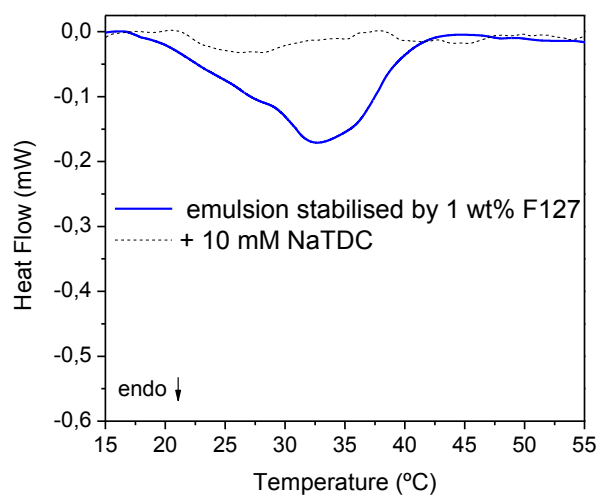
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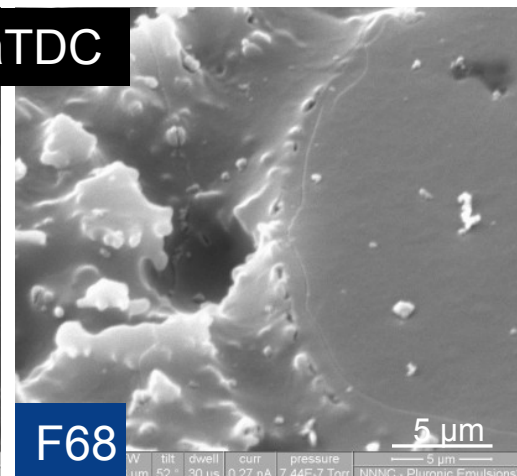
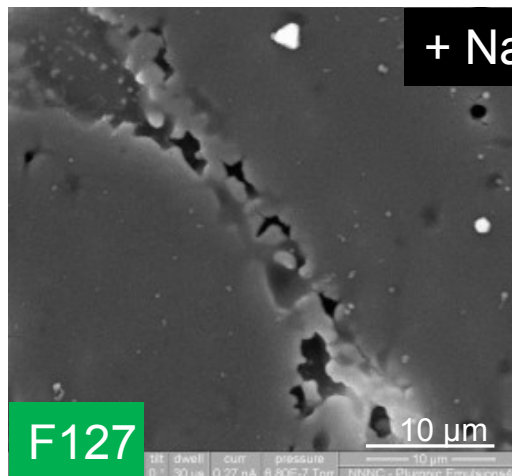
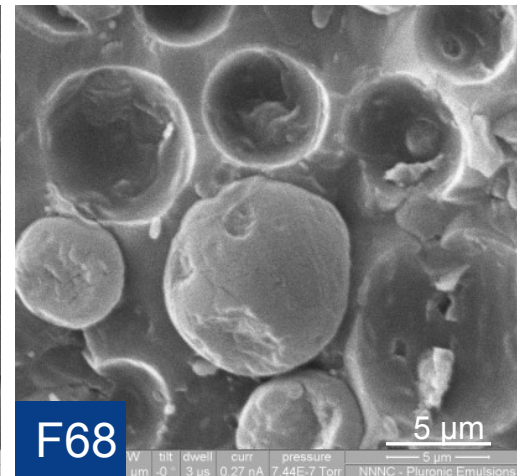
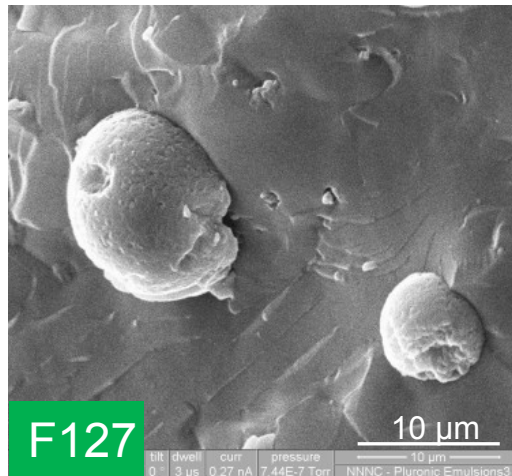
■ Micro-DSC



Results: Interactions in Pluronic-stabilised emulsions



- Cryo-SEM






Conclusions

- Pluronics seem to prevent BS from adsorbing onto the surface of oil droplets in emulsions due to a combination of **complexation** and **competitive adsorption**
- Pluronics are also **resistant to displacement** by BS from the oil-water interface
- The more hydrophobic and larger Pluronic (F127) better competes for the oil-water interface and interacts with greater amount of BS molecules
- These findings are relevant to the rational design in the control of lipid digestion

Further details

 A. Torcello-Gómez, J. Maldonado-Valderrama, A.B. Jódar-Reyes, T.J. Foster, Langmuir 29 (2013) 2520.

Further work

- Identifying functionalities of other potential (bio)polymers

Acknowledgements

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Thank you for your attention

