Research group 3.1.2: Active formulations and materials

Leading researcher: Prof. Slavka Tcholakova

Members of research team:

Prof. Ivanova

Assoc. Prof. Vinarov

Assoc. Prof. Burdziev

Assist. Prof. Lesov

Договор BG-RRP-2.004-0008-C01 за финансиране на проект „СОФИЙСКИ УНИВЕРСИТЕТ – МАРКЕР ЗА ИНОВАЦИИ И ТЕХНОЛОГИЧЕН ТРАНСФЕР (SUMMIT)“ по стълб 2 „Създаване на мрежа от изследователски висши училища“ в рамките на компонент „Иновативна България“ от Национален план за възстановяване и устойчивост към програмата за ускоряване на икономическото възстановяване и трансформация чрез наука и иновации

Appointed members of research group after competitions for recruitment of post-doctoral fellows:

N. Pagureva

L. Delforce (France)

B. Petkova

D. Gazolu-Rusanova

Z. Mitrinova

F. Mustan

Attracted students to prepare their MSc and BSc theses on the research program:

MSc K. Tzvetkova

MSc M. Stoeva (Moldova)

MSc V. Yordanova

BSc A. Todorova

BSc S. Paskova

BSc M. Alipieva

Main scope of the research program

Role of molecular surfactant structure on the formation, stability and rheology of multiphase systems (aggregates and mesophases in the bulk, foams, emulsions and drug delivery systems) with main focus on the eco-friendly, non-toxic surfactants

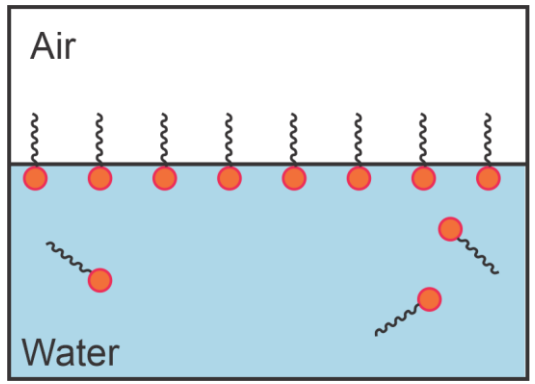
An important problem that the group's scientific program addresses is how to replace traditional surfactants with rapidly biodegraded and non-toxic substances

Surfactants

Hydrophobic part

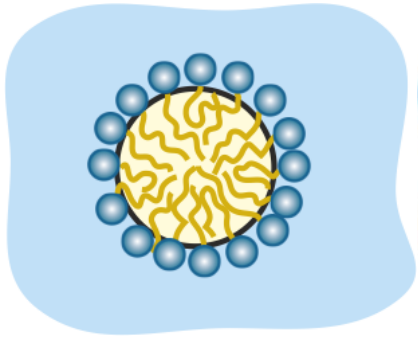
Hydrophilic head group

Adsorption on different interfaces

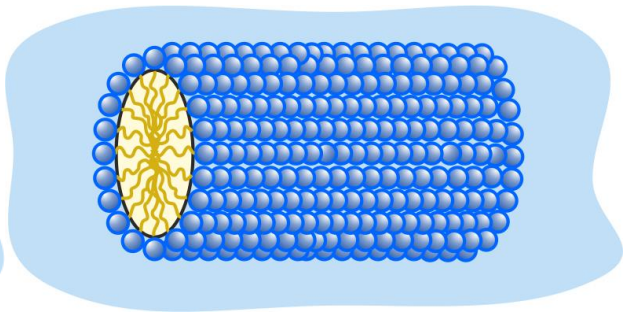


Formation of aggregates

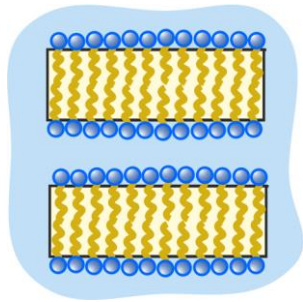
Spherical micelles



Cylindrical micelles



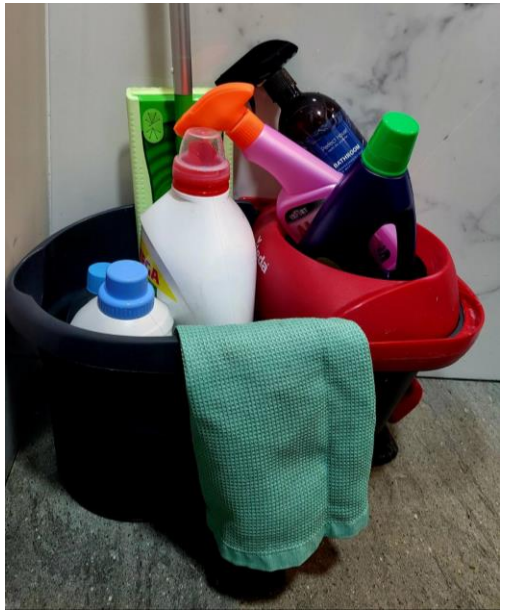
Lamellar phases



Surfactants used in practice: 18.8 billion tons for 2022; US$ 58.5 Bn in 2022

Household care (~ 45 %)

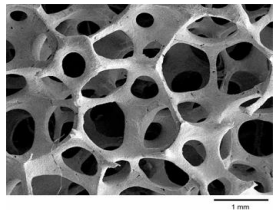
Industrial cleaning (~ 30 %)



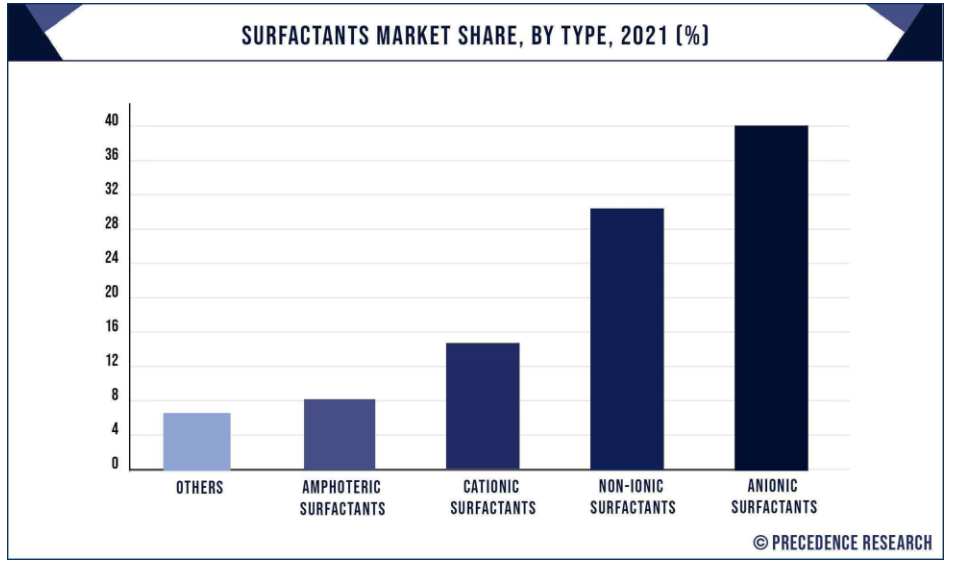
Personal care and cosmetics (~ 10 %)

Food and beverages (~ 10 %)

Other applications (~ 5 %)

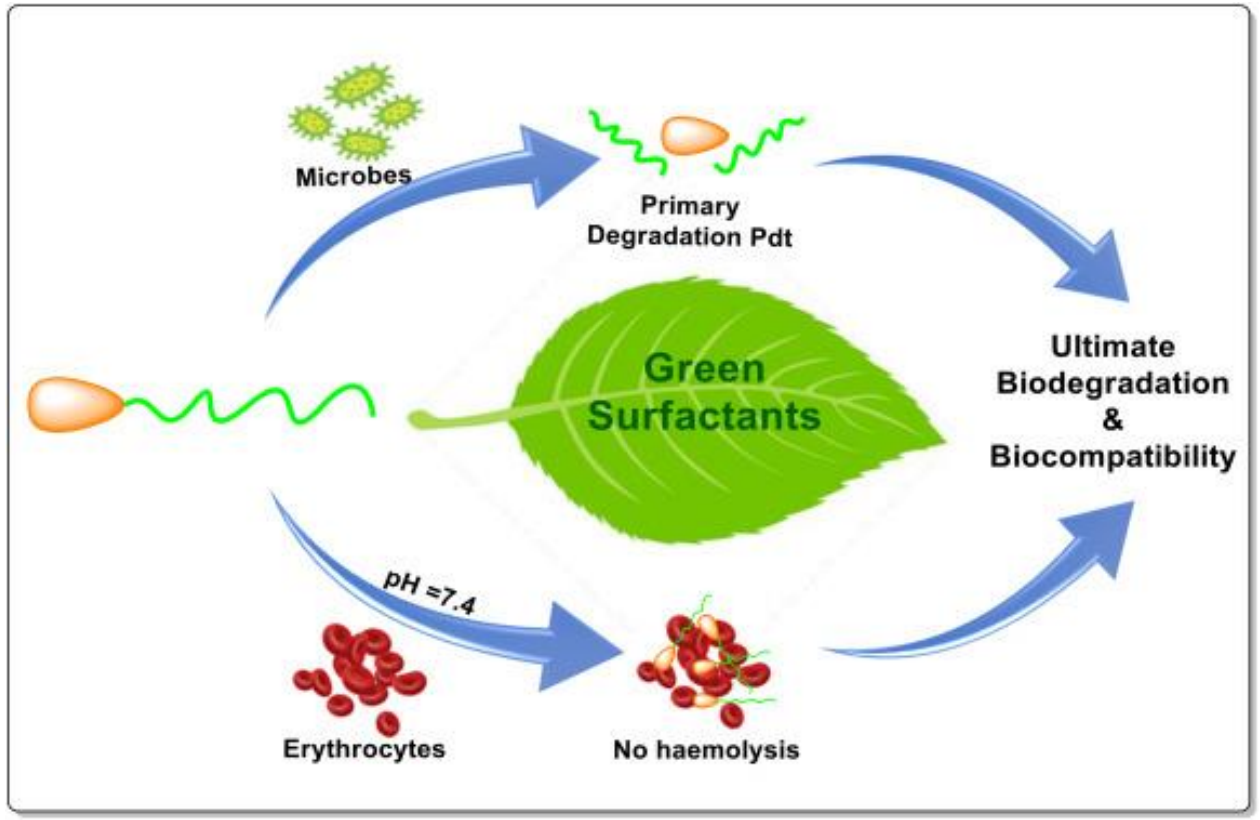


Type of used surfactants (Precedence research)



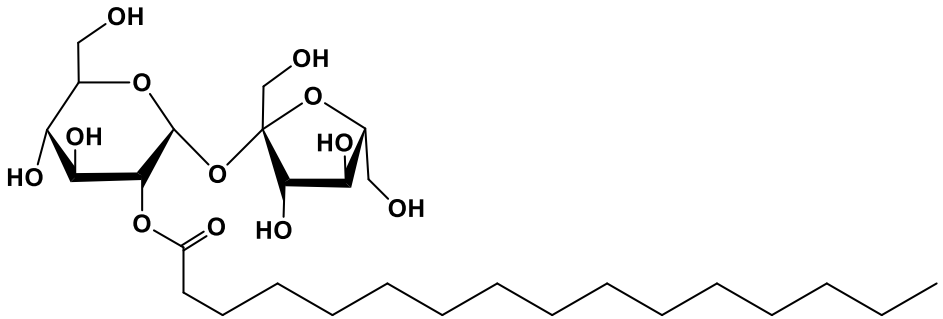
Biodegradable and non-toxic surfactants

Chowdhury et al. 2021

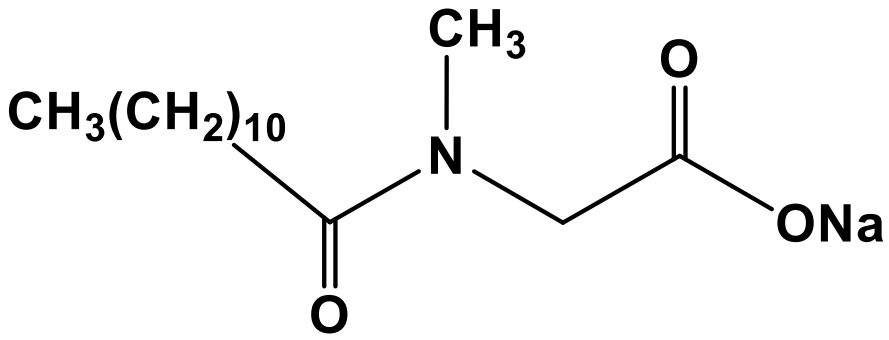


Studied surfactants in the current period

Alkyl sucrose esters

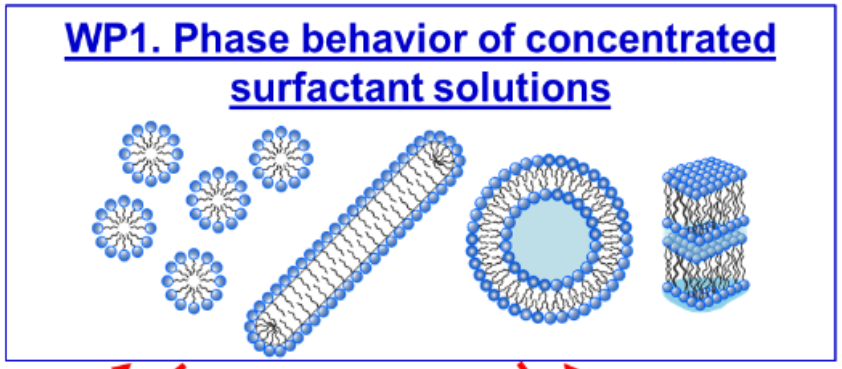


Alkyl sarcosinate



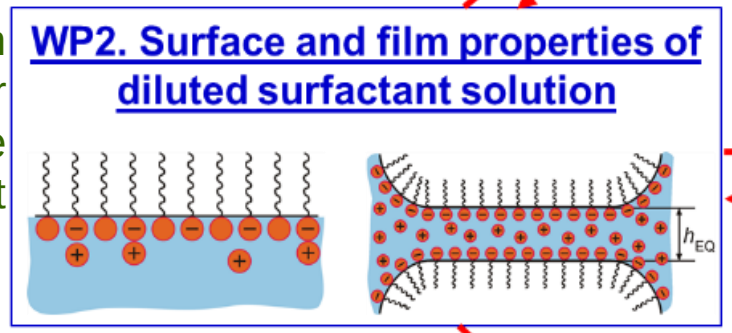
Work packages and major aims of the studies

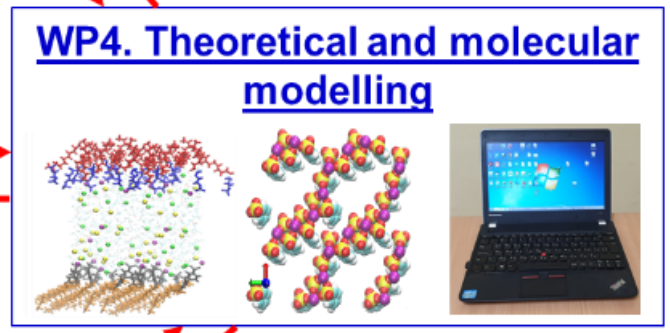
WP1: Clarify the effects of surfactants' molecular structure and concentration, electrolyte type and concentration, temperature and various additives on the type of formed aggregates.



WP1 & WP4: Relate the type of aggregates to rheological response of the formulations;
Predict the phase behaviour of concentrated surfactant solutions.

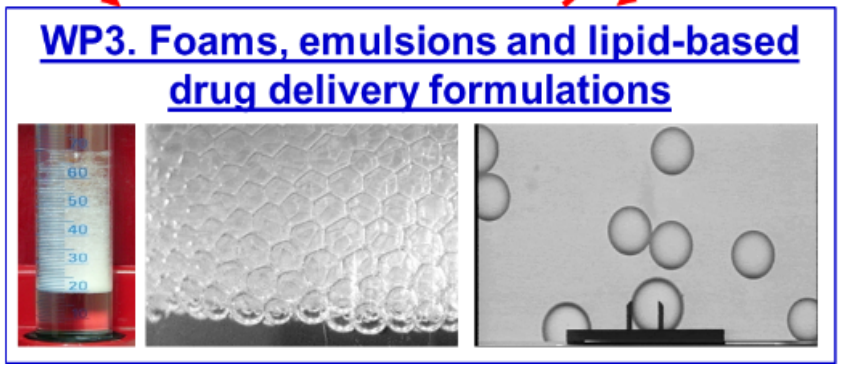
WP2: Relation between surfactant molecular structure and the properties of surfactant adsorption layers.





WP4: Molecular modelling of the main phenomena observed in concentrated surfactant solutions.

WP3: Clarify the role of hydrogen bonds on the rate of foam generation, and on the stability of the foams and emulsions formed;
Prepare new class of self-emulsifying lipid-based drug delivery systems



WP3 & WP4: Determine the effect of non-Newtonian behaviour of the aqueous solution on the rheological response of emulsions;
Develop a theoretical model for predicting the outcome of emulsification in non-Newtonian media

Summary

Tasks	Expected publications according to the proposal for the entire project	Prepared publications during first year of the project
1.1. Phase characterization	2 publications	1 manuscript submitted to JCIS 2 publications are under preparation
1.2. Rheological properties	1 publication	1 defended MSc Thesis and publication based on it is under preparation
1.3. Phase transitions	2 publications	2 publications are under preparation
2.1. Dynamic adsorption layers.	1 publication	1 manuscript submitted to COCIS
2.2. Equilibrium adsorption layers.	1 publication	1 publication is under preparation
2.3. Film properties	1 publication	
3.1. Foams	2 publications	1 manuscript published in CSA 1 publication is under preparation
3.2. Emulsions	2 publications	1 defended MSc Thesis and publication based on it is under preparation
3.3. Lipid-based drug delivery systems	1 publication and 1 patent application	
4.1. Molecular dynamics simulations	2 publications	
4.2. Theoretical model for concentrated solutions	1 publication	1 defended MSc Thesis and publication based on it is under preparation
4.3. Theoretical model for concentrated emulsions	1 publication	1 prepared manuscript which will be submitted to JCIS

Dissemination of the results from the project:

(1) S. Tcholakova, „Co-surfactants as a powerful tool for optimization of the formulation properties“, 12th World Surfactant Congress, 5-7 June 2023, Rome, Italy – keynote lecture.

(2) S. Tcholakova, „Physicochemical control of foam and emulsion properties“, XI Formulation Conference Lille, 3 - 6 July 2023, Lille, France – plenary lecture.

(3) S. Tcholakova, „Formation and rheology of emulsions and nanoemulsions”, UK Colloids Conference, 17 - 19 July 2023, Manchester, UK – keynote lecture.

(4) S. Tcholakova, „Formation and rheology of emulsions and nanoemulsions”, 20th July 2023, Research center of Unilever, Port Sunlight, UK – invited lecture.

(5) S. Tcholakova, „Биоразградими сърфактанти: предимства и предизвикателства при тяхното използване“ на 29 септември 2023 в рамките на ЕВРОПЕЙСКА НОЩ НА УЧЕНИТЕ, СОФИЯ.

(6) S. Tcholakova, „Physicochemical control of foam and emulsion properties“, 23th October 2023, IFPEN, France – invited lecture.

(7) N. Pagureva, M. Hristova, N. Burdziev, S.Tcholakova „Rheological properties and phase behavior of Sucrose Palmitate at different temperatures“, Научна сесия на Факултет по химия и фармация СУ ”Св. Климент Охридски” 21.11.2023.

Main achievements during year 1

- 6 postdocs appointed on the project
- 2 established researchers appointed on the project
- 3 MSc students and 3 BSc students attracted to work on the project
- 1 published manuscript in Colloids and Surfaces A (Q1)
- 2 submitted manuscripts to international journals in Q1 (JCIS and COCIS)
- 3 defended MSc Theses with excellent scores
- 1 plenary and 2 keynote lectures delivered on the international conferences
- 1 invited lecture in research institute of Unilever, UK and 1 invited lecture in IFPEN, France
- 6 signed collaboration contracts with international companies (Unilever, BASF, Wacker)
- 1 collaboration agreement with Prof. Hristo Svilenov (Ghent University, Belgium)
- Appointment for organization Formula XII conference in Sofia in 2025
- Participation in project 101157688 — SurfToGreen for topic: HORIZON-JU-CBE-2023-IA-05 — Development of scalable, safe bio-based surfactants, with an improved sustainability profile in Type of action: HORIZON JU Innovation Actions, selected for funding on 24/01/2024. Expected starting date 01/10/2024.
- Participation in project 101168870 — Edible Soft Matter for call: HORIZON-MSCA-2023-DN-01 — Doctoral Networks, which has been selected for funding on 21/03/2024. Expected starting date 01/09/2024.

Main scientific results obtained during first year of the project

WP1: Phase behavior of concentrated surfactant solutions

Manuscript under review in Journal of Colloid and Interface Science, IF = 9.9; Q1:

1. **Temperature response of sucrose palmitate solutions: Role of ratio between monoesters and diesters** by N. Pagureva, D. Cholakova, Z. Mitrinova, M. Hristova, N. Burdziev, S. Tcholakova

Manuscripts under preparation:

2. **Rheological response of sodium alkyl sacrosinates** by M. Stoeva, D. Gazolu-Rusanova, N. Burdziev, S. Tcholakova
3. **Role of surfactant chain length and degree of esterification for phase behaviour of alkyl sucrose ester solutions** by N. Pagureva, D. Cholakova, P. Borisov, S. Tcholakova
4. **Salts as triggers for changing phase behaviour of nonionic alkyl sucrose ester solutions** by N. Pagureva, D. Cholakova, P. Borisov, N. Burdziev, S. Tcholakova

Defended MSc Thesis with excellent score:

M. Stoeva: **Rheological response of sodium alkyl sacrosinates**

BSc Theses under preparation:

1. A. Todorova: **Phase behaviour of sodium lauroyl lactylate**
2. S. Paskova: **Role of second surfactant for phase behaviour of SLES mixtures in presence of sodium salts**

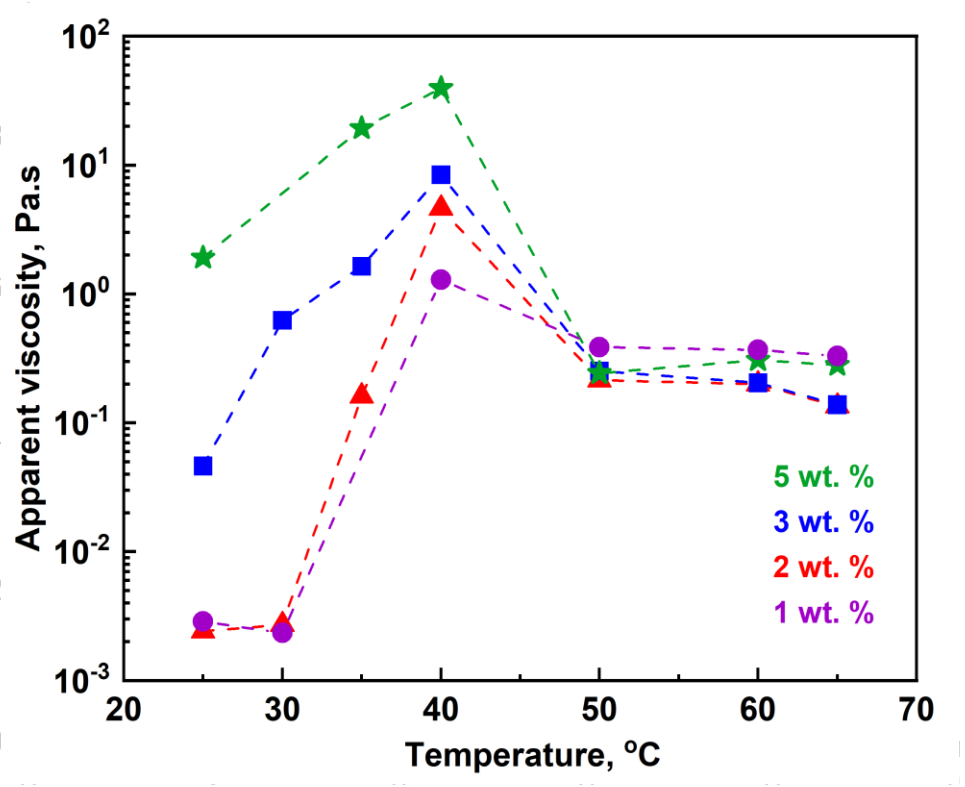
Temperature response of sucrose palmitate solutions: Role of ratio between monoesters and diesters

N. Pagureva, D. Cholakova, Z. Mitrinova, M. Hristova, N. Burdziev, S. Tcholakova

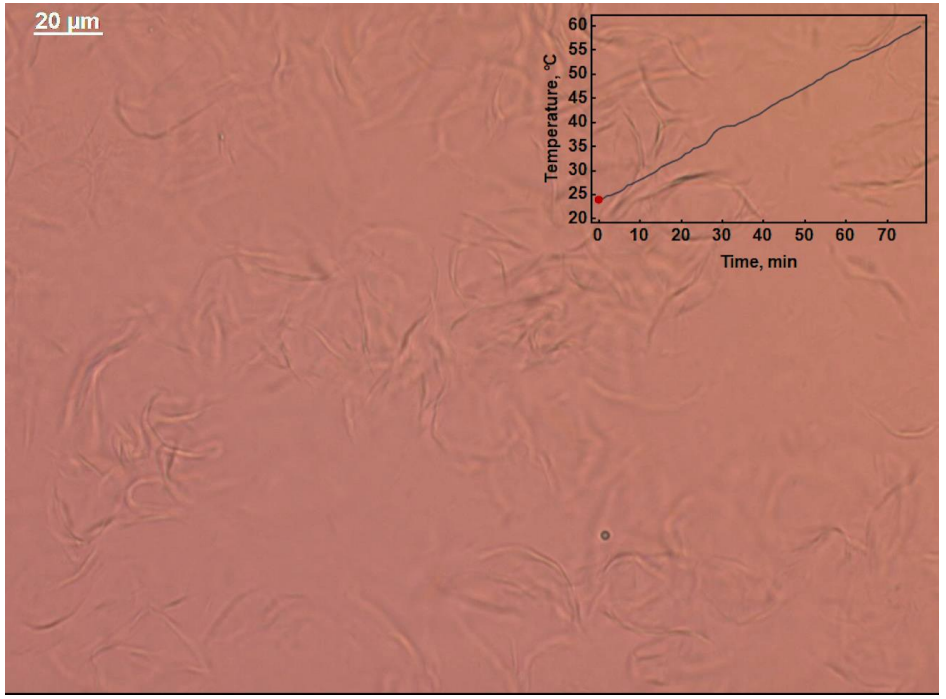
Under review in Journal of Colloid and Interface Science, IF = 9.9, Q1

Viscosity

Apparent viscosity vs temperature



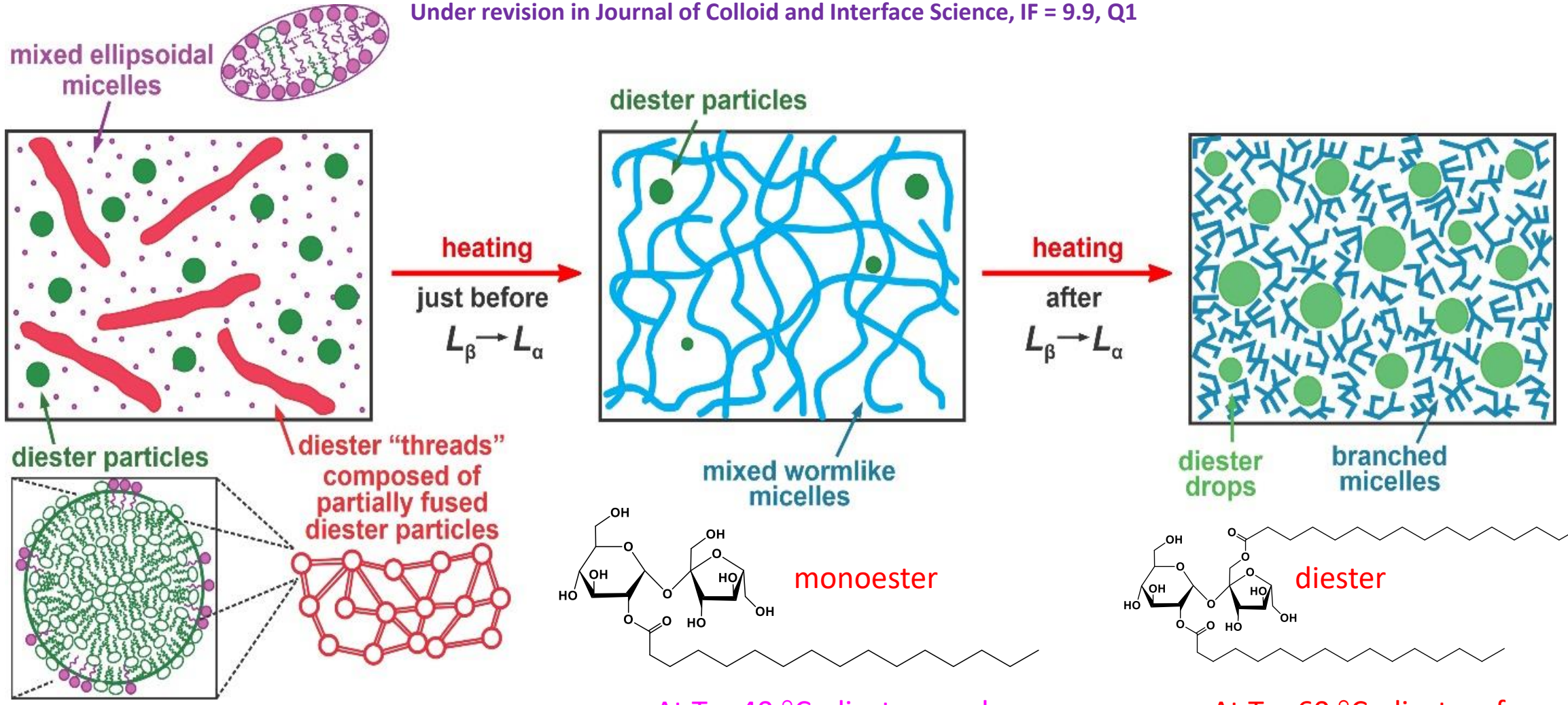
Phase behavior under microscope



Temperature response of sucrose palmitate solutions: Role of ratio between monoesters and diesters

N. Pagureva, D. Cholakova, Z. Mitrinova, M. Hristova, N. Burdziev, S. Tcholakova

Under revision in Journal of Colloid and Interface Science, IF = 9.9, Q1



At T ≈ 25 °C: diesters are arranged in particles; monoesters are in elongated ellipsoidal micelles.

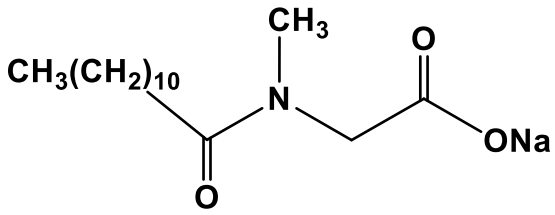
At T ≈ 40 °C: diesters and monoesters form long mixed wormlike micelles ⇒ very high solution viscosity

At T ≈ 60 °C: diesters form emulsion drops; monoesters form branched micelles and viscosity decreases

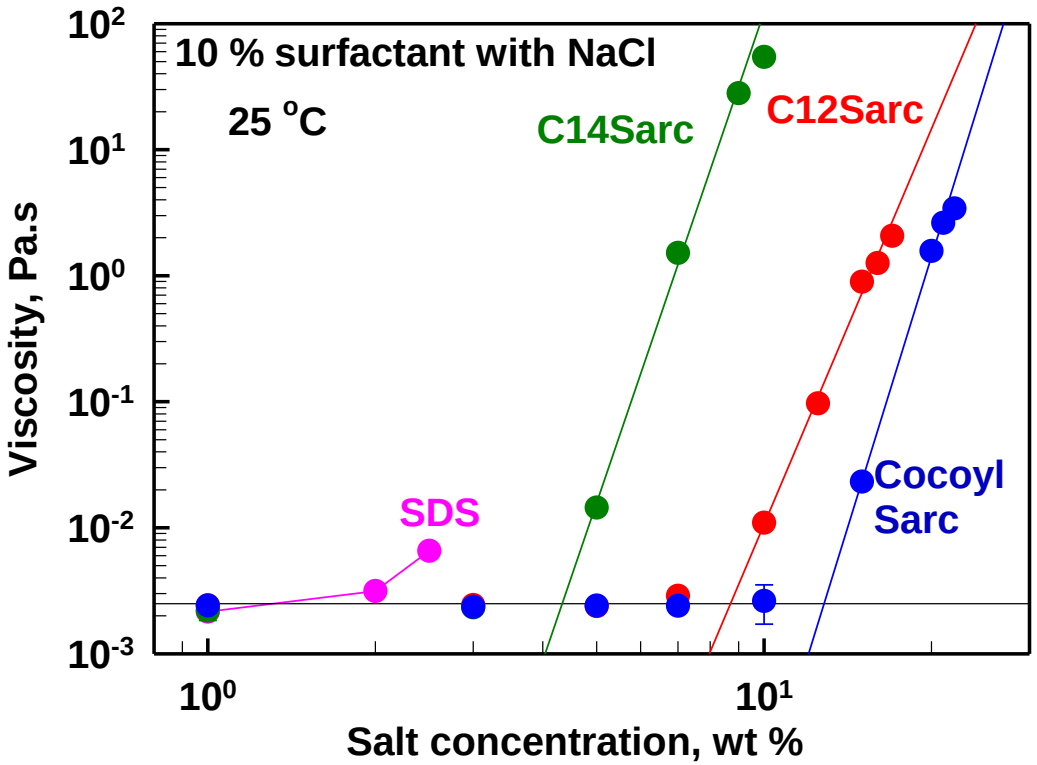
Rheological response of sodium alkyl sacrosinates

M. Stoeva, D. Gazolu-Rusanova, S. Tcholakova

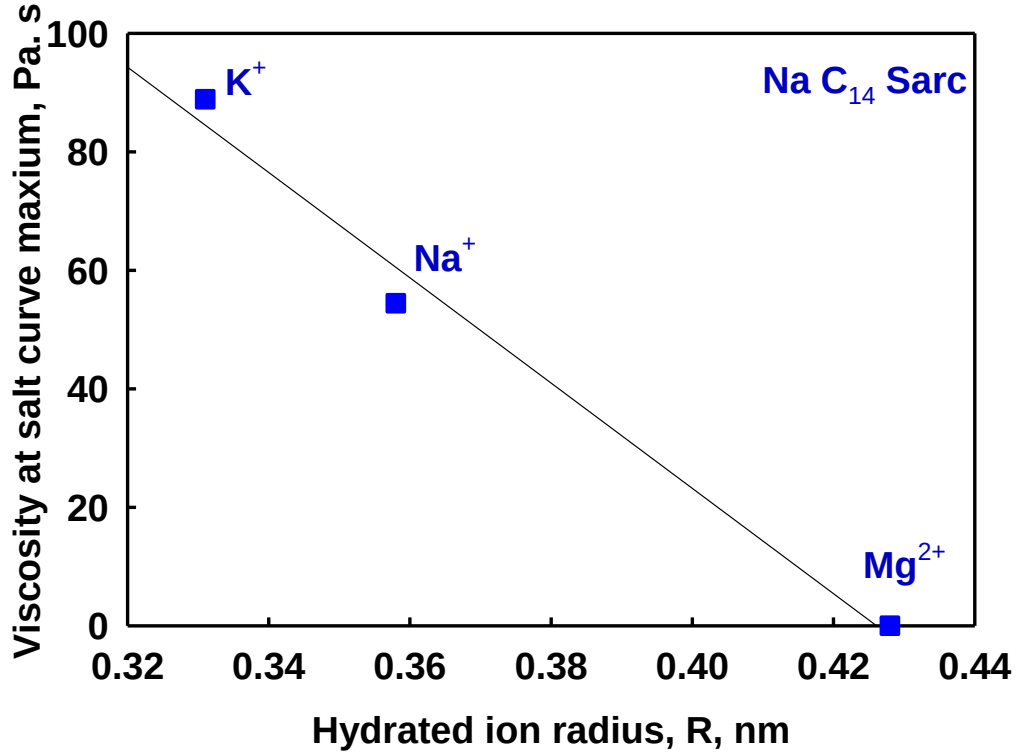
Defended MSc Thesis of M. Stoeva with excellent score
(manuscript under preparation)



Viscosity vs NaCl concentration



Maximal viscosity vs hydrated ion radius of counterion



The increase of salt concentration decreases the electrostatic repulsion between the head groups of alkyl sarcosinates, leading to formation of wormlike micelles in the solutions.
Further increase of salt concentration leads to precipitation of alkyl sarcosinate salts, instead of formation of branched micelles (as the conventional anionic surfactants, such as SLES).

WP2: Surface and film properties of diluted surfactant solutions

Invited manuscript under review in Current Opinion in Colloid and Interface Science, IF = 8.9; Q1:

1. Bubble size and foamability: role of surfactants and hydrodynamic conditions by S. Tcholakova and B. Petkova

Manuscript under preparation:

2. Surface, film and foam properties of sodium alkyl sarcosinate solutions by B. Petkova, S. Tcholakova

WP3: Foams, emulsions and lipid-based drug delivery formulations

Published manuscript in Colloids and Surfaces A, 611 (2024) 133844; IF = 5.2; Q1:

1. Role of temperature and urea for surface and foam properties of nonionic surfactants with dodecyl alkyl chain by L. Delforce and S. Tcholakova

Manuscripts under preparation:

2. **Formation and stability of soybean oil emulsions from sucrose solutions of nonionic surfactants** by K. Tzvetkova, Z. Vulkova, S. Tcholakova

3. **Stability of foams formed from solutions of nonionic surfactants: Role of surfactant tail and method for foam generation** by L. Delforce and S. Tcholakova

Defended MSc Thesis with excellent score:

K. Tzvetkova: **Formation and stability of soybean oil emulsions from sucrose solutions of nonionic surfactants**

BSc Thesis under preparation:

Mira Alipieva: **Foamability of biodegradable anionic surfactants**

Role of temperature and urea for surface and foam properties of nonionic surfactants with dodecyl alkyl chain

L. Delforce, S. Tcholakova

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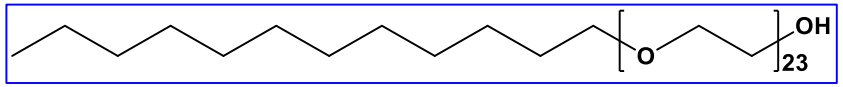

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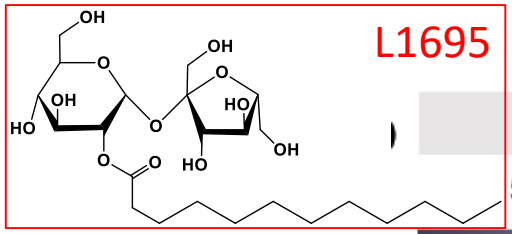
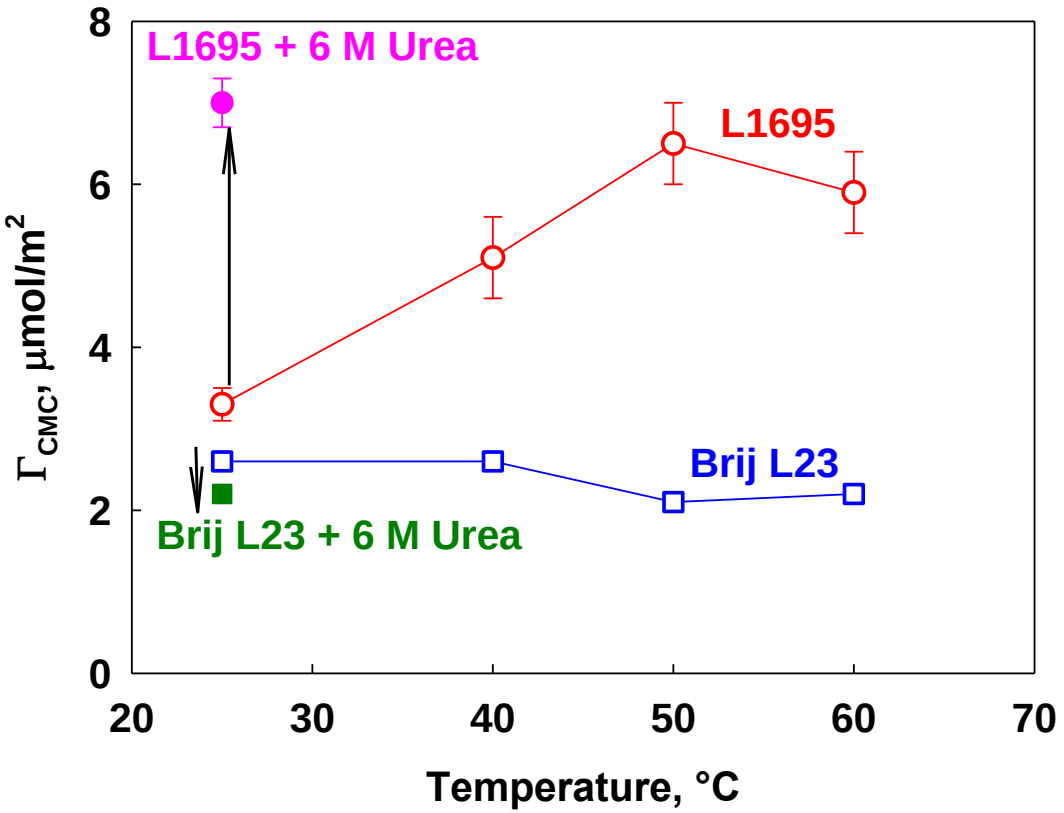
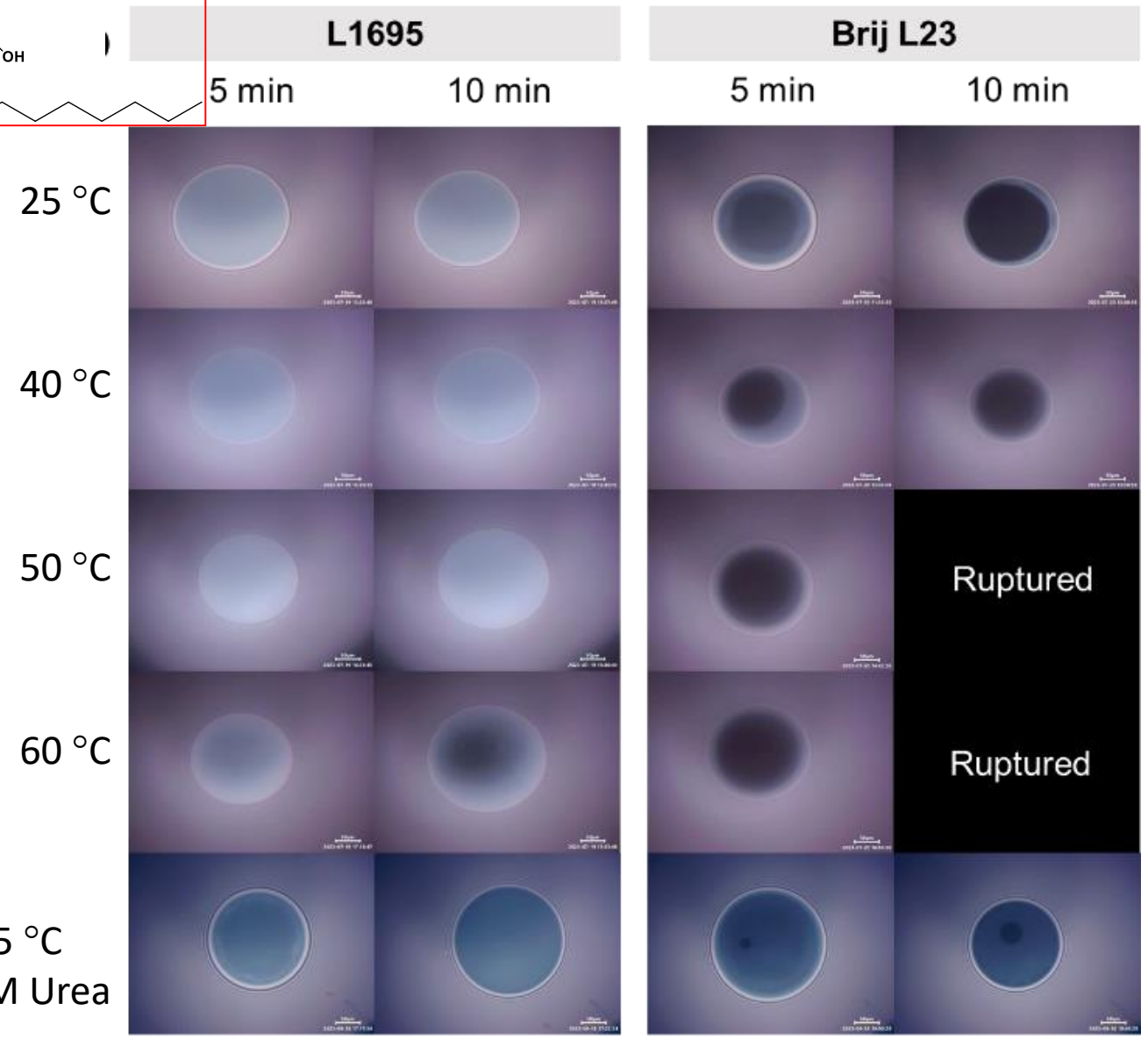


Surfactant adsorption



Colloids and Surfaces A, 611 (2024) 133844, IF = 5.2, Q1

Film properties

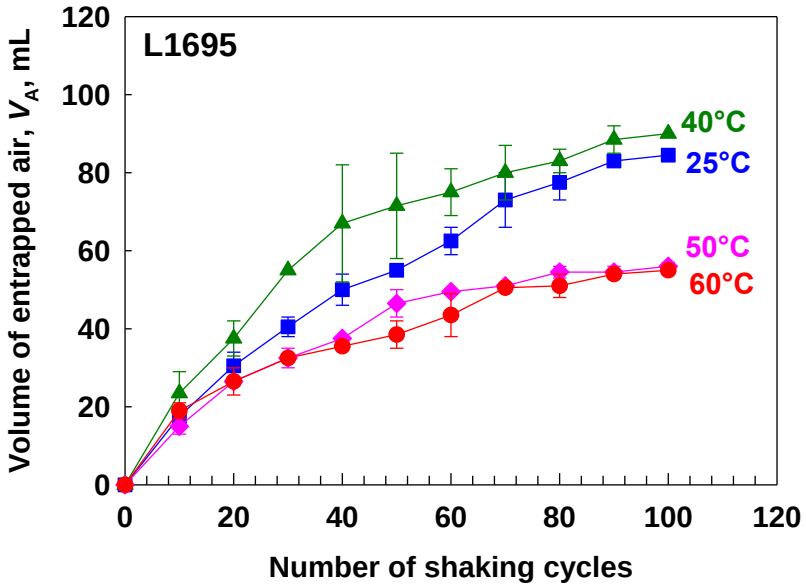


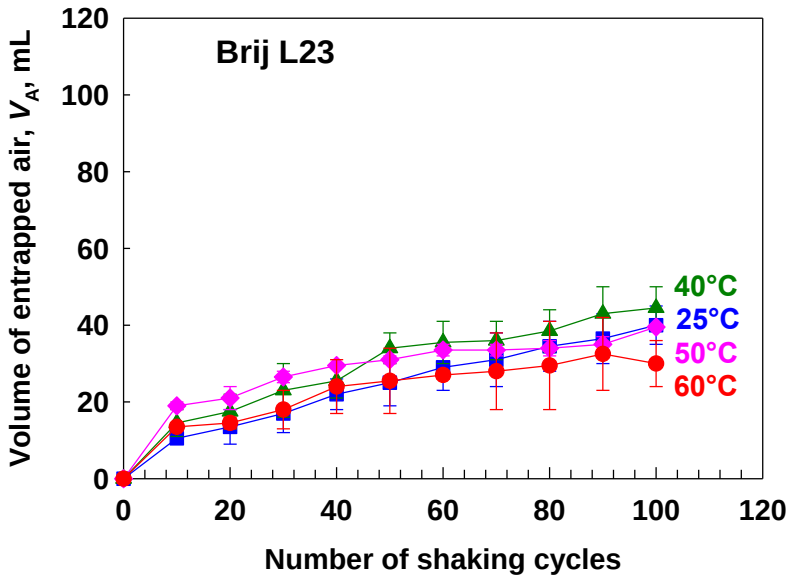
Role of temperature and urea for surface and foam properties of nonionic surfactants with dodecyl alkyl chain

L. Delforce, S. Tcholakova

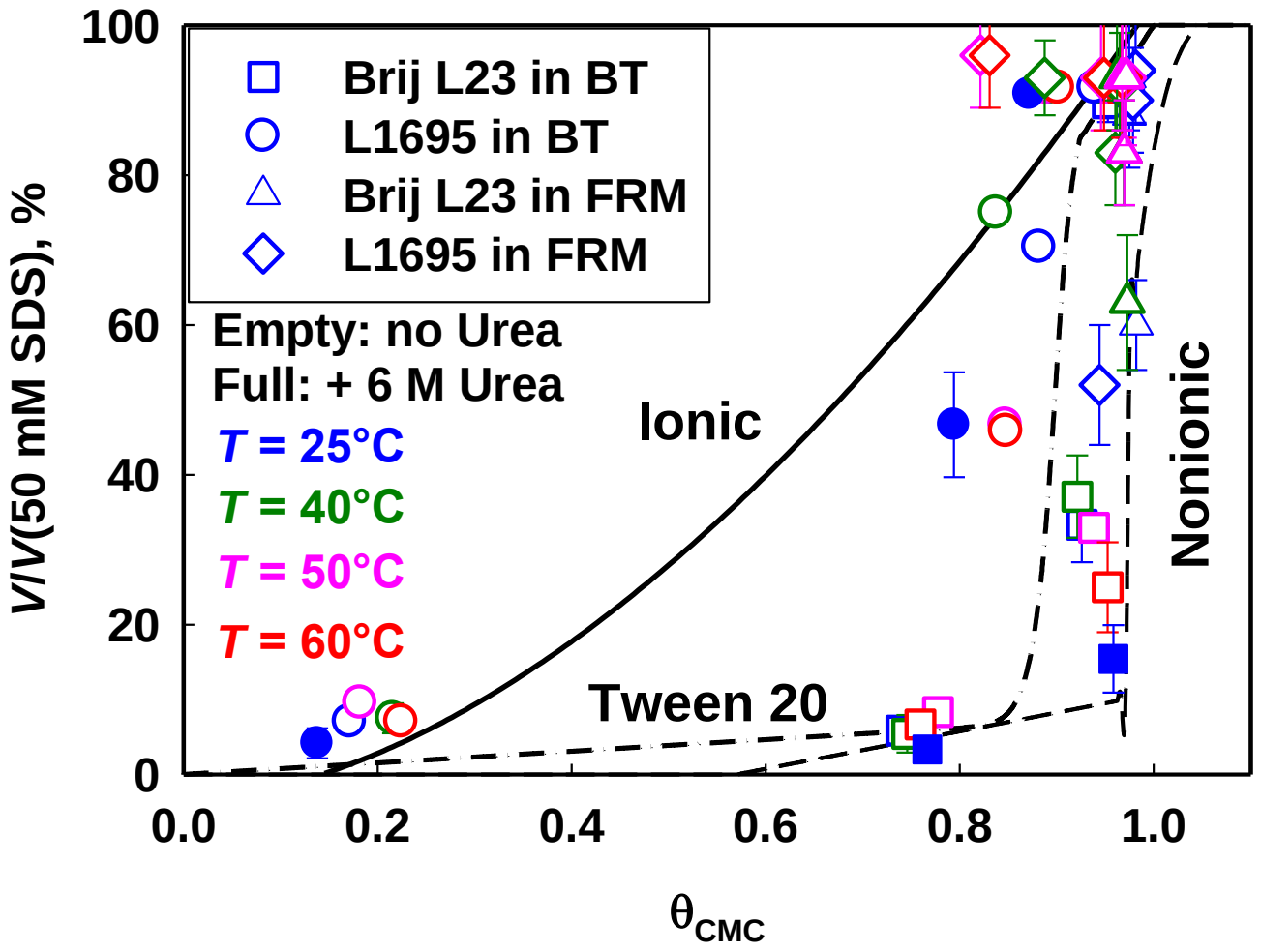
Colloids and Surfaces A, 611 (2024) 133844, IF = 5.2, Q1

Foamability





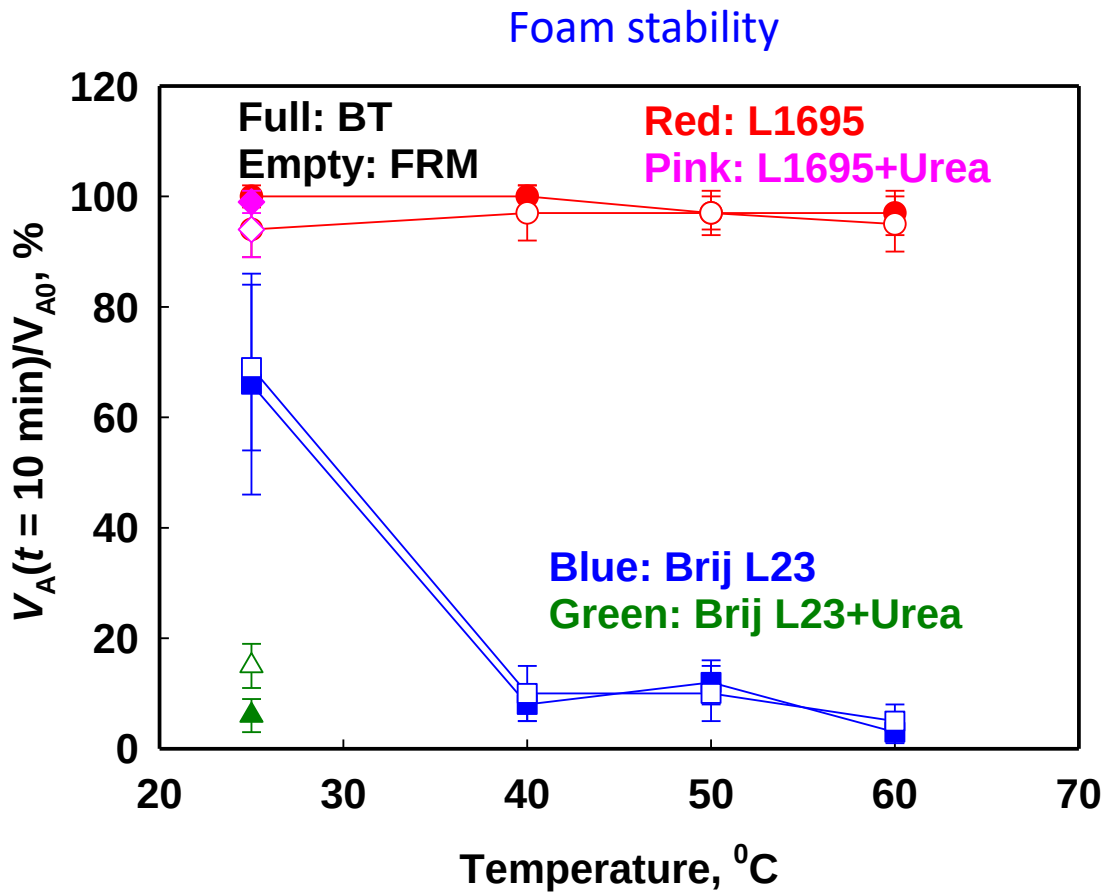
Foamability vs dynamic surface coverage

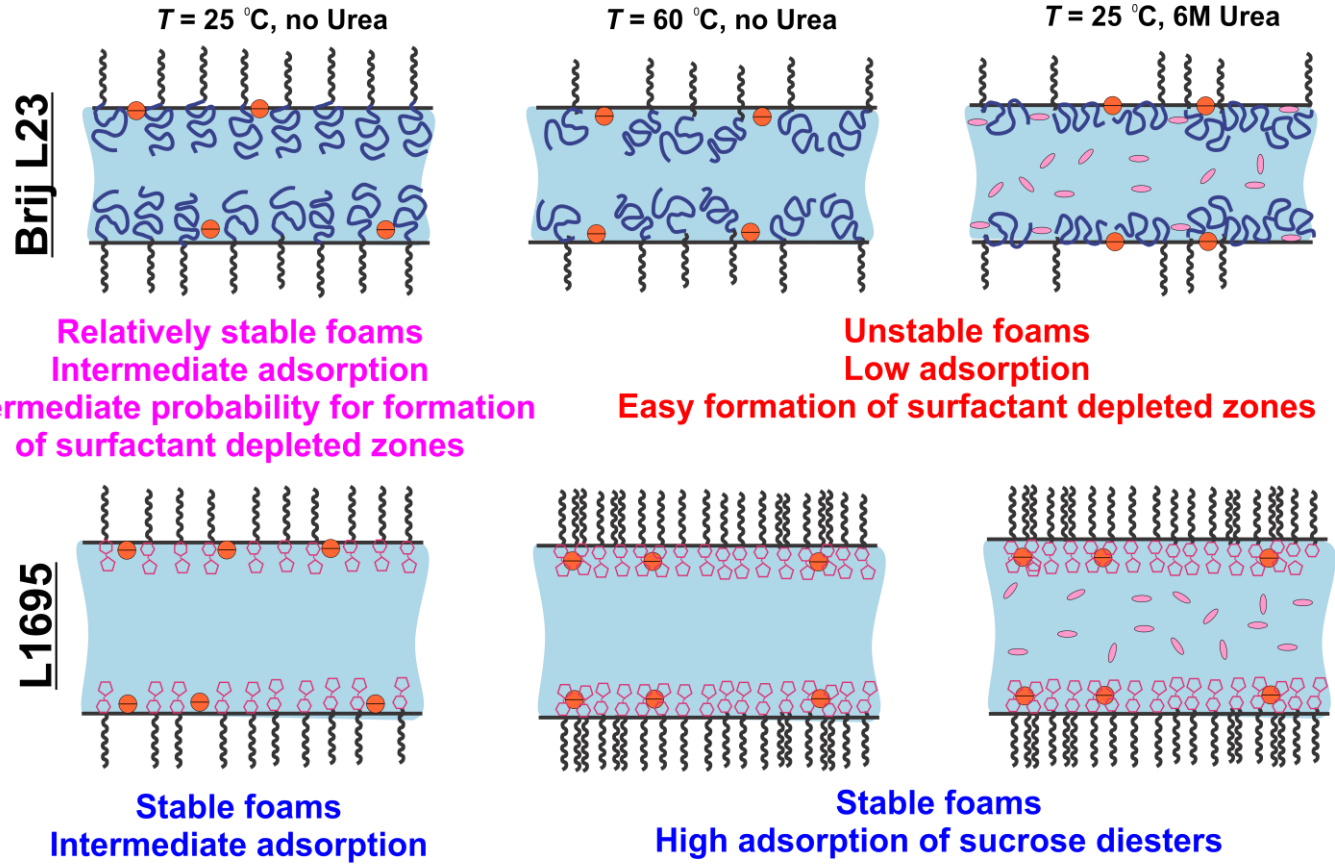


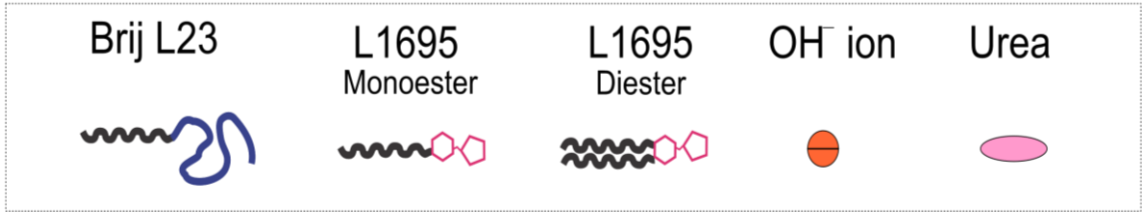
Role of temperature and urea for surface and foam properties of nonionic surfactants with dodecyl alkyl chain

L. Delforce, S. Tcholakova

Colloids and Surfaces A, 611 (2024) 133844, IF = 5.2, Q1







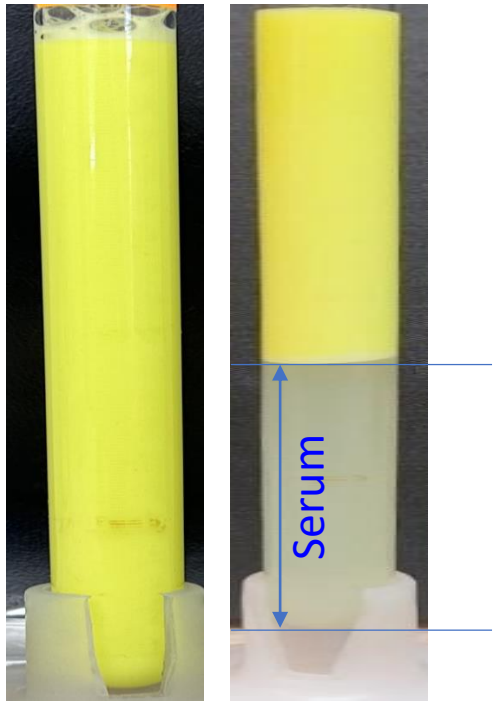
Formation and stability of soybean oil emulsions from sucrose solutions of nonionic surfactants

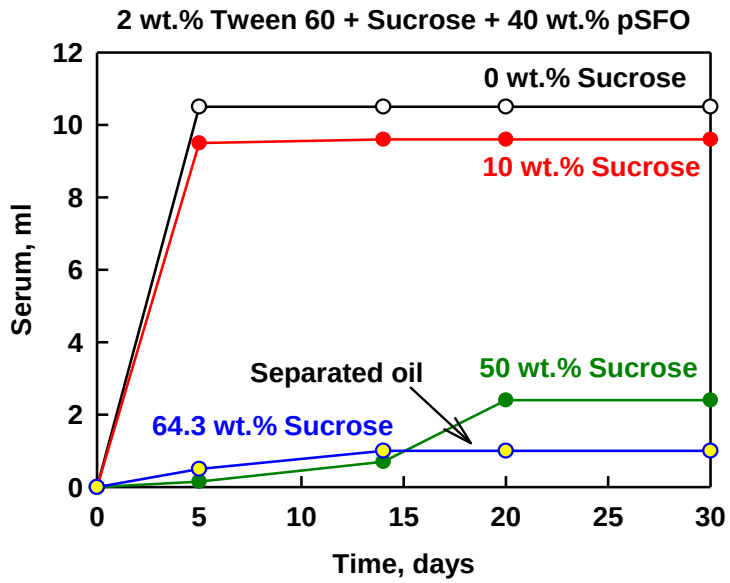
K. Tzvetkova, Z. Vulkova, S. Tcholakova

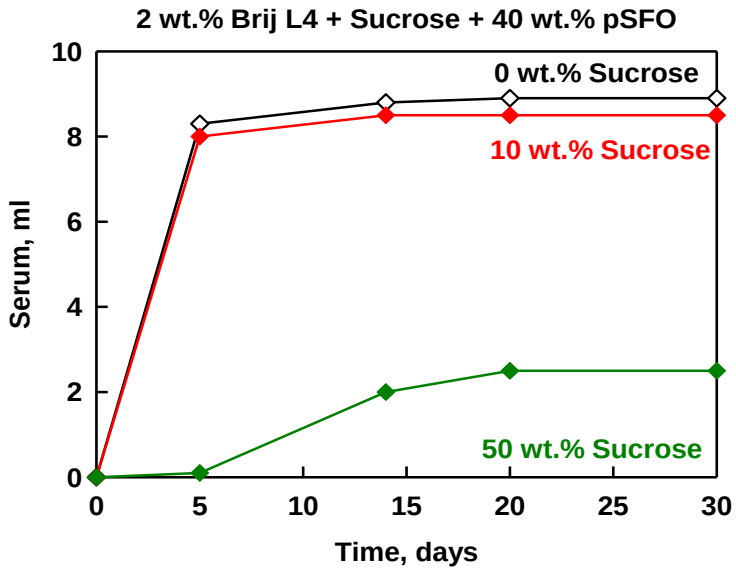
Defended MSc Thesis of K. Tzvetkova with excellent score; manuscript under preparation

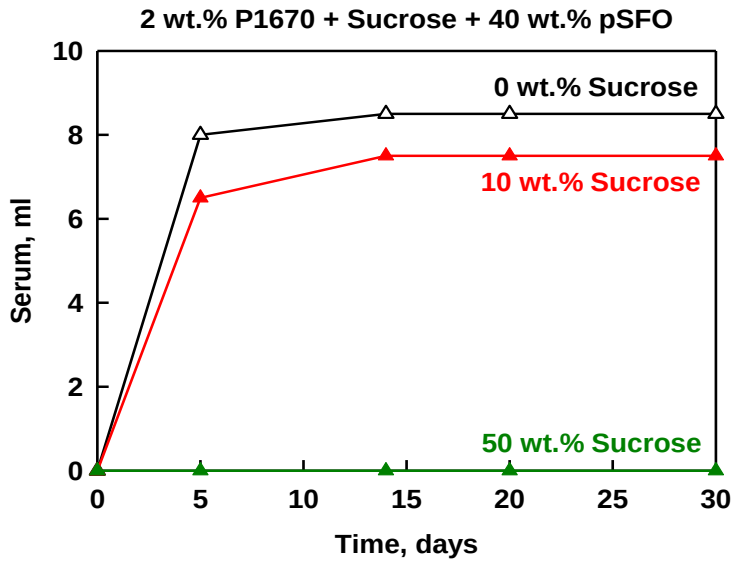
Initial emulsion

After storage









Emulsion stability passes through a maximum while increasing sugar concentration in the aqueous solution.

The emulsion of 40 wt. % SFO, obtained from 2 wt.% P1670 with added 50 wt.% sugar, remained stable for more than 30 days.

WP4: Theoretical and molecular modelling

Defended MSc Thesis with excellent score:

V. Yordanova: **Role of co-ions for phase behaviour of SLES solutions**

Manuscripts under preparation:

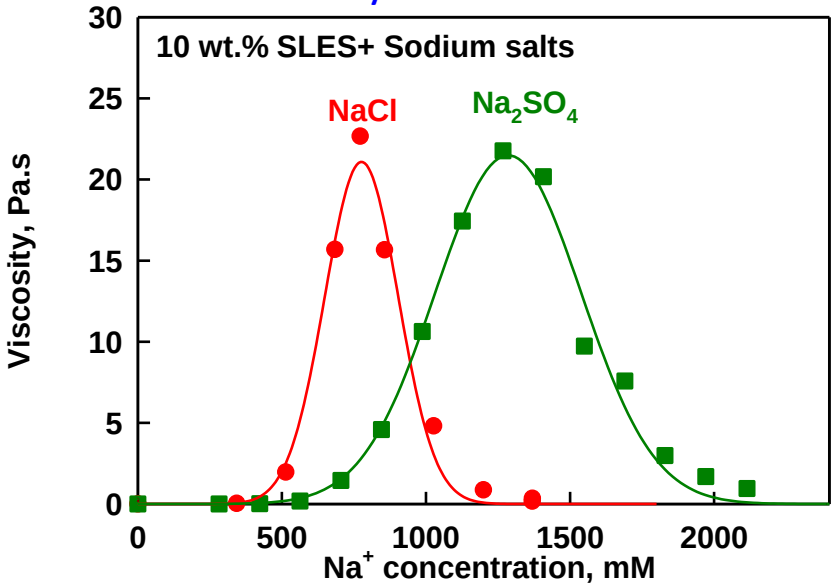
1. **Emulsification of silicone oils in Newtonian and non-Newtonian media of wormlike micelles** by I. Lesov and S. Tcholakova
2. **Role of co-ions for phase behaviour of SLES solutions** by V. Yordanova, Z. Mitrinova and S. Tcholakova
3. **Role of counterions for phase behavior of SLES-CAPB mixtures** by Z. Mitrinova and S. Tcholakova

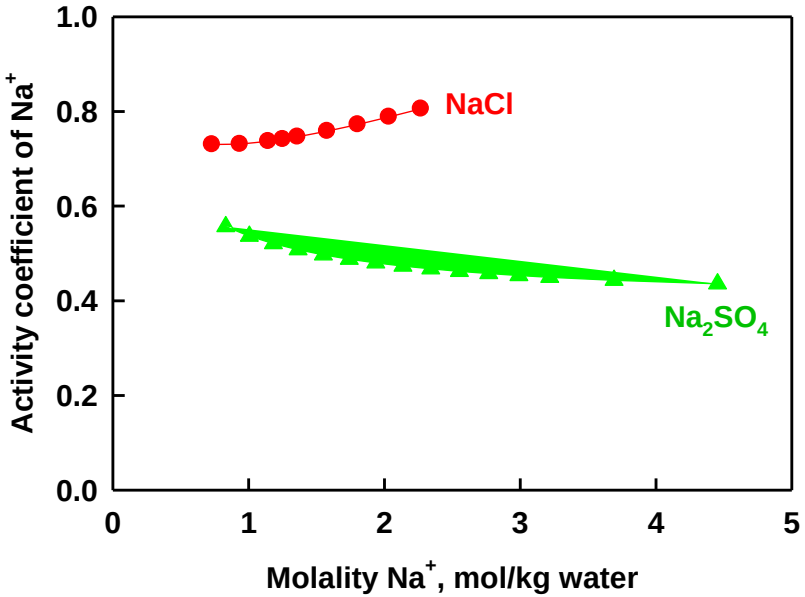
Role of co-ions for phase behaviour of SLES solutions

V. Yordanova, Z. Mitrinova, S. Tcholakova

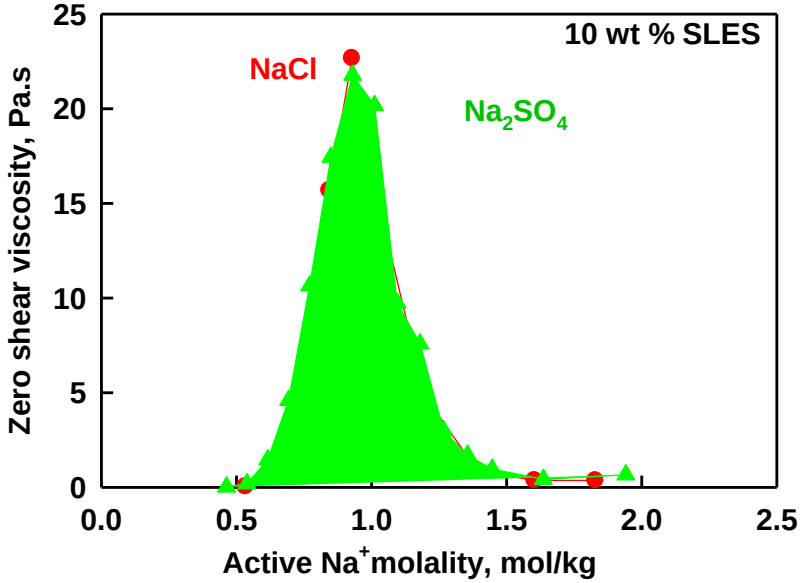
Defended MSc Thesis of V. Yordanova with excellent score
(manuscript under preparation)

Viscosity vs Na^+ concentration





Viscosity vs Na^+ activity



Individual activity coefficients

Khoshkbarchi&Vera 1996

$$\ln \gamma_i = -\frac{A_x z_i^2 I_x^{1/2}}{1+9I_x^{1/2}} + \frac{B_{xi} I_x^{3/2}}{1+9I_x^{1/2}} + D_{xi} \ln\left(1+9I_x^{2/3}\right)$$

New theoretical model is developed to account for the activity coefficients of Na^+ ions coming from different salts.

Universal viscosity curve as a function of Na^+ activity for SLES with different salt mixtures is obtained using the new model.

Emulsification of silicone oils in Newtonian and non-Newtonian media of wormlike micelles

I. Lesov, S. Tcholakova

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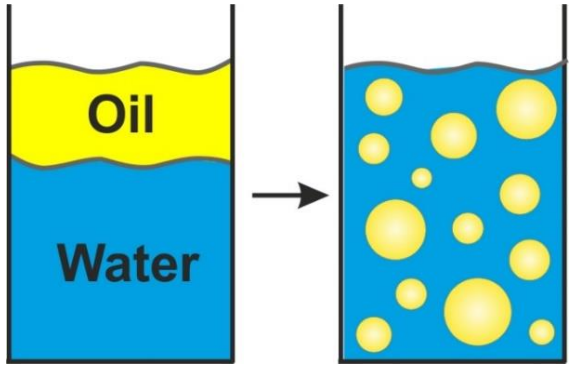
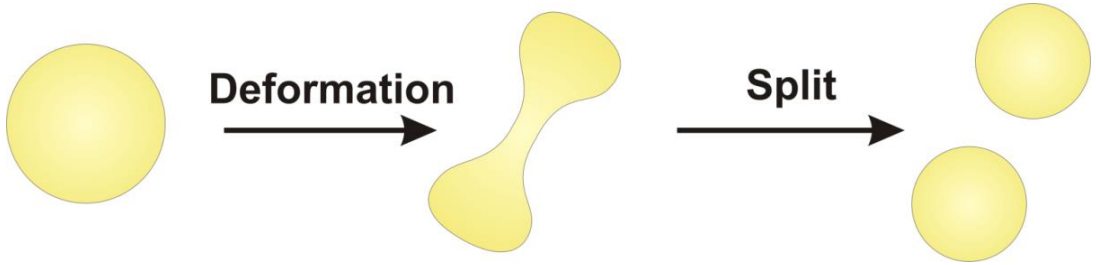
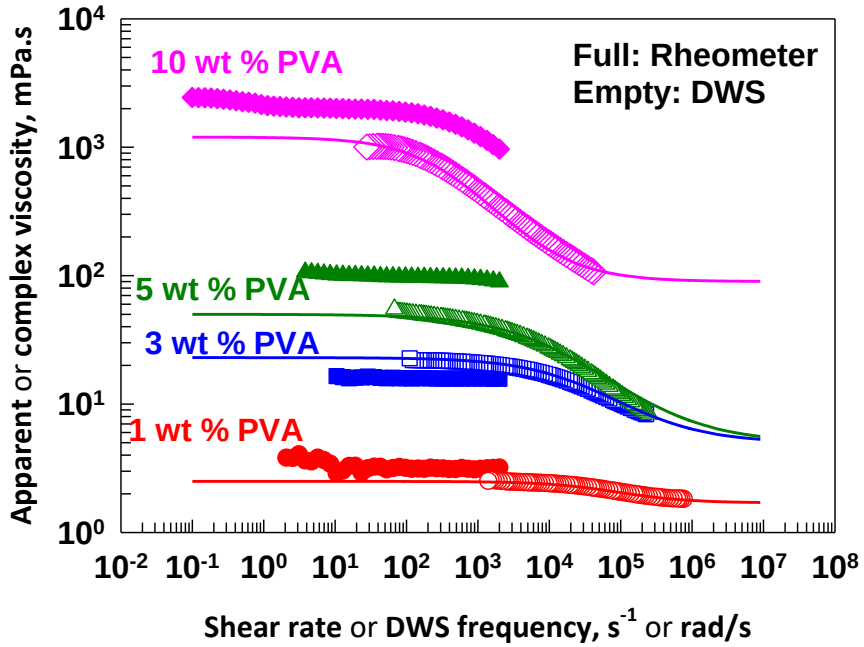
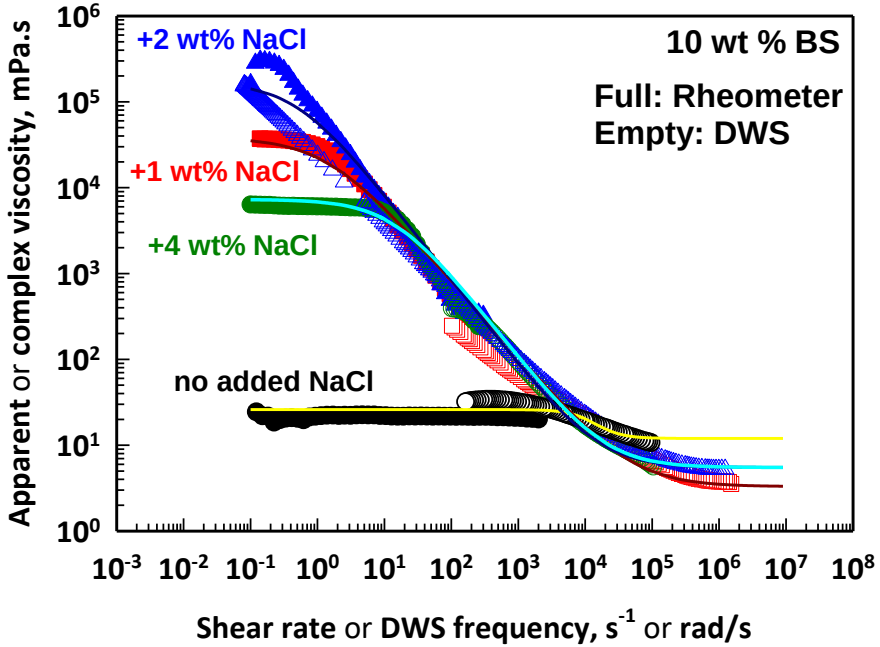




Nearly Newtonian solutions



Non-Newtonian solutions



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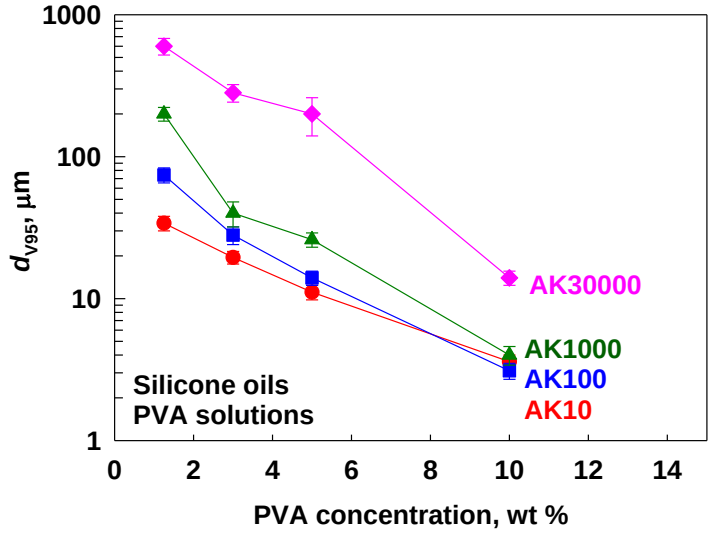
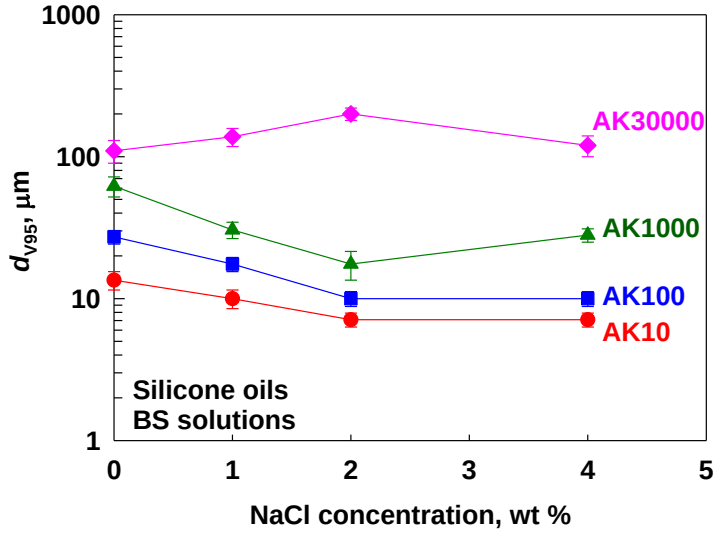
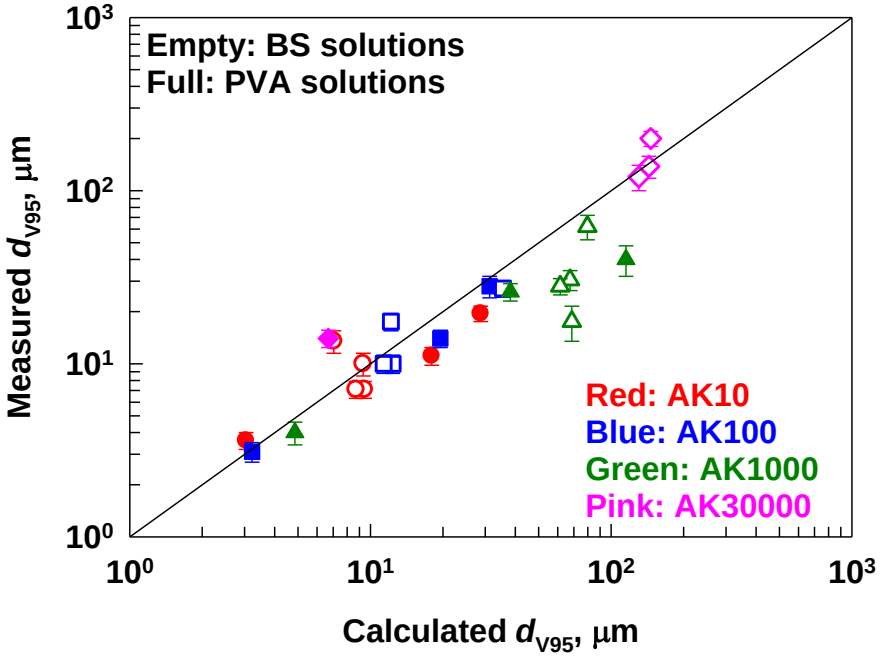
Drop sizes
in nearly Newtonian solutions



Drop sizes
in non-Newtonian solutions



Measured vs Predicted drop size



$$\frac{\eta_{C0}-\eta_{C\infty}}{1+\left(k_C\dot{\gamma}\right)^{n_C}}\dot{\gamma}=C_6\frac{\sigma}{d_V}+C_7\frac{\eta_{D0}-\eta_{D\infty}}{1+\left(k_DC_8\dfrac{\left(\varepsilon d_V\right)^{1/3}}{d_V}\right)^{n_D}}C_8\frac{\left(\varepsilon d_V\right)^{1/3}}{d_V}$$

New equation for predicting the maximum drop size in emulsions formed in Newtonian and non-Newtonian media is derived and verified experimentally.

Thank you for your attention!

ДОГОВОР BG-RRP-2.004-0008-C01 ЗА ФИНАНСИРАНЕ НА ПРОЕКТ „СОФИЙСКИ УНИВЕРСИТЕТ – МАРКЕР ЗА ИНОВАЦИИ И ТЕХНОЛОГИЧЕН ТРАНСФЕР (SUMMIT)“ ПО СТЪЛБ 2 „СЪЗДАВАНЕ НА МРЕЖА ОТ ИЗСЛЕДОВАТЕЛСКИ ВИСШИ УЧИЛИЩА“ В РАМКИТЕ НА КОМПОНЕНТ „ИНОВАТИВНА БЪЛГАРИЯ“ ОТ НАЦИОНАЛЕН ПЛАН ЗА ВЪЗСТАНОВЯВАНЕ И УСТОЙЧИВОСТ КЪМ ПРОГРАМАТА ЗА УСКОРЯВАНЕ НА ИКОНОМИЧЕСКОТО ВЪЗСТАНОВЯВАНЕ И ТРАНСФОРМАЦИЯ ЧРЕЗ НАУКА И ИНОВАЦИИ