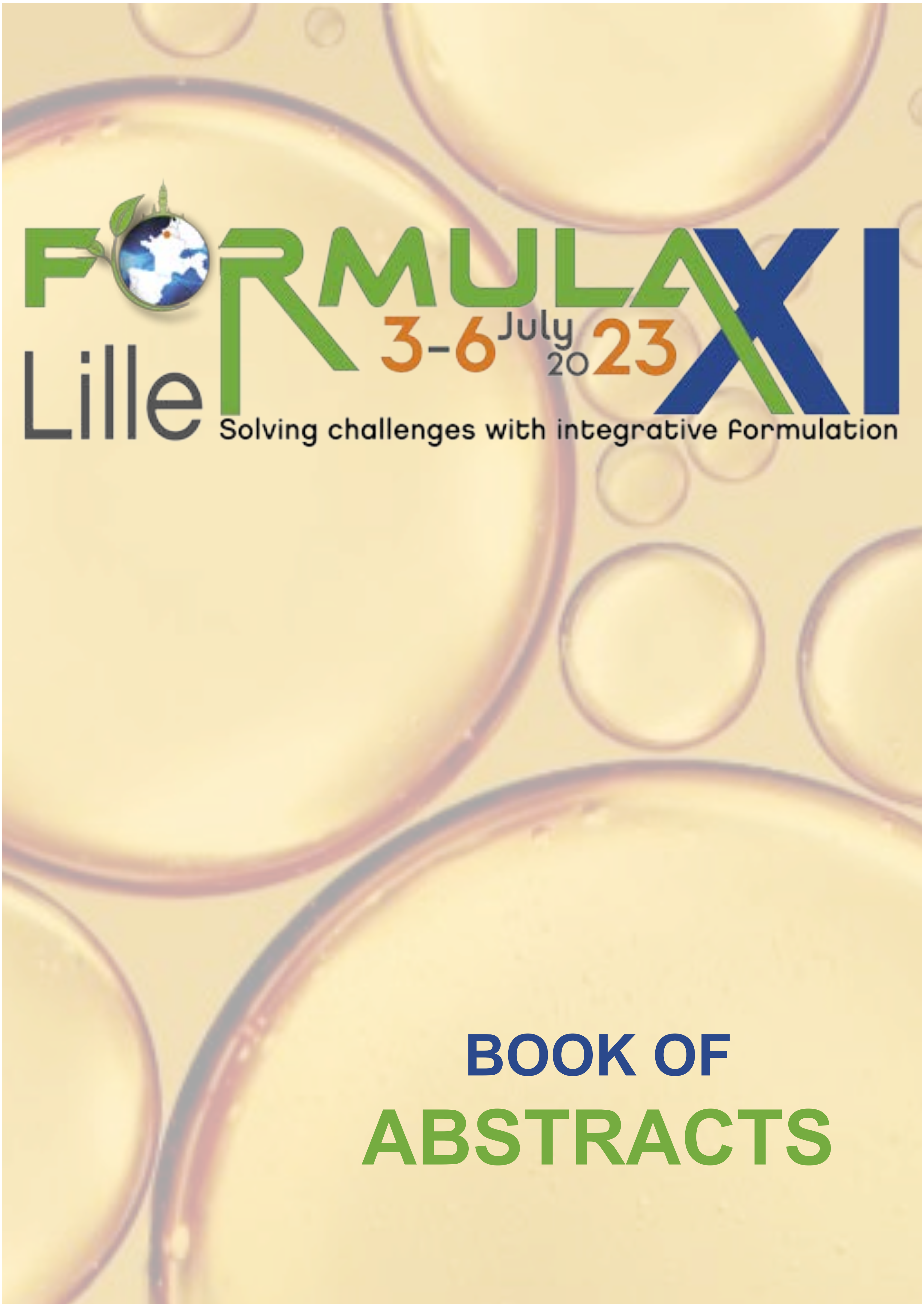

FORMULA XI

Lille

3-6 July 2023

Solving challenges with integrative formulation

BOOK OF ABSTRACTS

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Welcome

Dear Colleagues

The world is changing, the way we look at chemistry is changing, consumer habits are changing. Formulation is at the heart of these concerns and, as an essential part of our daily lives, it must adapt and provide viable solutions in line with these changes. Energy, sustainability, environment, decarbonation, safety, must now be integrated into the development of new raw materials and formulations. Ingredients considered as « cleaner and more sustainable alternatives » and new formulations, which must be developed with a minimum of raw materials, wherever possible biobased, while maintaining performance, create new challenges.

The Formula conferences are a privileged place for researchers and industrials to meet and discuss. They bring together all those involved in the exciting, multidisciplinary, complex but extremely rich field of Formulation, whether they are manufacturers of formulated products, suppliers of specialty chemicals or researchers and academics in applied colloidal physical-chemistry or polymers in solution who are striving to design functional compounds or elucidate the underlying physicochemical mechanisms to understand and provide knowledge and guidance to the formulator.

This not-to-be-missed event has been a great success since its creation by the French Chemical Society (SCF). It covers all aspects of Formulation Science and Technology, from the most fundamental and theoretical to the most applied. The title of the conference « Solving challenges with integrative formulation » is intended to emphasize that scientific discoveries and technical innovation are the driving forces behind bringing new products to the market, meeting the ever-changing needs of customers and the planet.

The Formula XI conference hold in Lille, France, from 3-6 July 2023, following the Formula X conference in Manchester in 2019, Formula IX in Beijing in 2017 and Formula VIII in Barcelona in 2015.

The invited lectures, the different and numerous presentations, as well as the poster sessions, cover all areas of Formulation Science and Technology and provide new cutting-edge aspects.
Thank you for attending this nice event!

Véronique Nardello-Rataj
Chairwoman of the organizing Committee

FORMULA XI
Lille 3-6 July 2023
Solving challenges with integrative formulation

Formulation Conference Lille
– 3 to 6 July 2023 –

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Special issue in Colloids and Surfaces A: Physicochemical and Engineering Aspects

This special issue compiles original works presented in the FORMULA XI congress that will take place in Lille between July 3-6, 2023. FORMULA has been held for almost 35 years and its original idea was to cover the different fields of formulation (paints, cosmetics, food, pharmaceuticals, home care, etc.) with the participation of people from academia and industry. Colloidal physical chemistry, and more specifically the formulation of dispersed systems such as emulsions, foams, suspensions and their characterization are recurrent topics. Moreover, the ecological transition represents a challenge in the field to replace petroleum-based raw materials and incorporate more environmentally friendly ingredients in formulated products.

Keywords:
Formulation, Colloidal systems, Surfactants, Foams, Emulsions, Thin Films

Manuscript submission information:
You are invited to submit your manuscript at any time before the submission deadline. For any inquiries about the appropriateness of contribution topics, please contact Dr Carlos Rodriguez Abreu via cranqb@cid.csic.es.

The journal's submission platform (Editorial Manager®) will be available for receiving submissions to this Special Issue from **07-Jul-2023**. Please refer to the Guide for Authors to prepare your manuscript and select the article type of "**VSI: Formula XI**" when submitting your manuscript online. Both the Guide for Authors and the submission portal could be found on the Journal Homepage here: https://www.sciencedirect.com/journal/colloids-and-surfaces-a-physicochemical-and-engineering-aspects

Manuscript Submission Deadline: 07-Dec-2023

CONFERENCE PROGRAM

MONDAY 3th JULY

12:00	**Registration desk opens**	
14:00 **14:30**	Opening of the Conference – Welcome Speech	**Véronique Nardello-Rataj** Formula XI Chairwoman **Franck Dumeignil** Vice-President of the University of Lille **Jordi Esquena** Chariman IAB
PLENARY LECTURE		**Chair: Véronique Nardello-Rataj**
14:30 **15:30**	**Science driven formulation for sustainable & desirable cosmetic products (PL1)**	**Odile Sonneville-Aubrun** L'Oréal R&I, France – Advanced Research Physical-Chemistry & Deposition Science / Science & Process of Formulation
ORAL PRESENTATIONS		**Chair: Véronique Nardello-Rataj**
15:30 **15:55**	**Accelerate the development of cosmetic ingredients thanks to sensory/in vivo correlated and predictive physicochemical characterizations (OC 01)**	**Florian Laubé** Seppic Research & Innovation Castres, France
15:55 **16:15**	**Formulation and applicability of fully and homogeneous topical Pickering emulsions, and description of the phenomena that occurred within the system (OC 02)**	**Aurélie Asdrubal** University Le Havre Normandie URCOM UR 3221, Le Havre, France
16:15 **16:35**	**Hybrid systems combining hyaluronic acid and liposomes for local drug delivery: how liposome characteristics govern the microstructure and their release (OC 03)**	**Florence Agnely** University Paris-Saclay, Institut Galien Paris-Saclay, Orsay, France
16:35-17:00 **COFFEE BREAK**		
17:00 **17:20**	**Water-in-water novel systems for the encapsulation of active components (OC 04)**	**Jordi Esquena** IQAC-CSIC, CIBER-BBN Jordi Girona, Barcelona, Spain
17:20 **17:40**	**Gradient poly(2-oxazoline)s as a new class of biocompatible emulsifiers: Structure-property relationships and cosmetic application (OC 05)**	**Valentin Bardoula** Ghent University, Ghent, Belgium University of Lille, France
17:40 **18:00**	**Methodology and preliminary steps to develop an innovative bioinspired cosmetic active ingredient (OC 06)**	**Maria Vieytez** University Cote d'Azur, INC, Nice, France - University of Lille, France Shiseido Group, Ormes, France
18:00 **18:20**	**Theoretical and experimental approaches of extraction. Developing multiple solvents systems and deep eutectic solvents for the optimisation of extraction and solubilization of volatile or non-volatile compounds (OC 07)**	**Nicolas Papaiconomou** University Côte d'Azur, INC Nice, France

KEYNOTE		Chair: Véronique Nardello-Rataj
18:20 18:50	Sustainable, Nutritious, Plant based and/or Dairy? How Nestlé is addressing its future formulation challenges using advanced & traditional approaches (K01)	Tim J Wooster Nestlé R&D, Lausanne, Switzerland
19:00 – 20:30 POSTER SESSION AND WELCOME RECEPTION		

TUESDAY 4th JULY

PLENARY LECTURE		**Chair: Malcolm Faers**
8:30 **9:30**	**Physicochemical control of foam and emulsion properties (PL 02)**	**Slavka Tcholakova** Faculty of Chemistry & Pharmacy, Sofia University, Bulgaria
KEYNOTE		**Chair: Malcolm Faers**
9:30 **10:00**	**Non-aqueous foams stabilized by crystalline particles: from design to applications (K02)**	**Anne-Laure Fameau** INRAE Nantes, France
ORAL PRESENTATIONS		**Chair: Malcolm Faers**
10:00 **10:20**	**Elaboration and characterization of capsules from the polymerization of Pickering emulsions stabilized by cellulose nanocrystals (OC 08)**	**Véronique Schmitt** CRPP, University Bordeaux Pessac, France
10:20 – 10:40 **COFFEE BREAK**		
ORAL PRESENTATIONS		**Chair: Ronald Marquez**
10:40 **11:00**	**Pickering emulsions stabilized by oppositely charged particles (OC 09)**	**Mathis Benyaya** University Claude Bernard Lyon 1, LAGEPP, Villeurbanne, France
11:00 **11:20**	**The mechanism of bilayer permeation of oil-soluble substances with bile salt (OC 10)**	**Oda Minaru** Faculty of Science and Technology, Tokyo University of Science Tokyo, Japan Lion corporation Tokyo, Japan
11:20 **11:40**	**Diclofenac recovery from aqueous solutions by emulsion liquid membranes (OC 11)**	**Adriana Corona Rodríguez** Universidad De Guanajuato, México
11:40 **12:00**	**Morphology controlled nanomaterials to navigate mucosal barriers (OC 12)**	**Kawthar Bouchemal** Chimie Paris Tech, University PSL Paris, France
12:00 **12:20**	**Exploring ageing, network stresses and gravitational stability in model suspension formulation systems (OC 13)**	**Rui Cheng** University of Bristol, Bristol, UK Bayer AG, Monheim, Germany
12:30 – 14:00 **LUNCH**		
PLENARY LECTURE		**Chair: Alain Durand**
14:00 **15:00**	**Applications of the COSMO-RS and COSMOplex methods in formulation science (PL 03)**	**Andreas Klamt** Senior scientist fellow, Dassault Systems, Germany
ORAL PRESENTATIONS		**Chair: Alain Durand**
15:00 **15:20**	**Formulation optimisation assisted by AI-based optimisation algorithms (OC 14)**	**Thomas Galeandro-Diamant** DeepMatter, Lyon, France
15:20 **15:40**	**A novel hybrid artificial intelligence approach for optimizing the formulation of calcined clay cements (OC 15)**	**Yassine El Khessaimi** University of Limoges, Limoges, France

15:40 – 16:00 **COFFEE BREAK**		
ORAL PRESENTATIONS		**Chair: Jean-François Dechezelles**
16:00 **16:20**	**Immobilization of organic nuclear waste in Pickering emulsions: formulation and characterization (OC 16)**	**Jordan Bassetti** University of Lille, UCCS, Lille, France CEA, Univ Montpellier, Marcoule
16:20 **16:40**	**Sustainable Liquid-liquid extraction of metals using hydrotropes as extractants (OC 17)**	**Thomas Zemb** Institut de Chimie Séparative de Marcoule, France
16:40 **17:00**	**Characterization of aqueous two-phase systems for arsenic removal (OC 18)**	**Guadalupe Falcón Millán**
17:00 **17:20**	**Energy storage systems: Optimize formulation and fabrication (OC 19)**	**Yassine Nagazi** Formulaction, Toulouse, France
17:20 **17:40**	**Replacing a PFAS surfactant for a biodegradable blend in a highly oxidative triiodide solution used for gold etching in semiconductor manufacturing (OC 20)**	**Rogelio Gomez** Technic France Saint-Denis La Plaine, France
KEYNOTE		**Chair: Jean-François Dechezelles**
17:45 **18:15**	**Advanced Formulation from an industry perspective – trends and new strategies, methods, and tools to scope with new challenges (K03)**	**Frank Runge** Vice President – Research Program Leader Advanced Formulation and Manager BASF SE, Germany
19:00 (Departure by bus) – 24:00 (Return to the Hotel) **DINNER EVENT**		

WEDNESDAY 5th JULY

PLENARY LECTURE		**Chair: Jordi Esquena**
8:30 **9:30**	**Green high performance solvents and related formulations (PL 04)**	**Werner Kunz** Regensburg University, Institute of Physical and Theoretical Chemistry, Regensburg, Germany
ORAL PRESENTATIONS		**Chair: Jordi Esquena**
9:30 **9:50**	**Influence of low water content on the thermo-physical properties of deep eutectic solvent choline chloride-urea and its application to colloidal dispersions (OC 21)**	**Véronique Peyre** Sorbonne University, Paris, France
9:50 **10:10**	**The application of sustainable surfactant-free microemulsions as reaction solvents (OC 22)**	**Evamaria Hofmann** Regensburg University, Institute of Physical and Theoretical Chemistry, Regensburg, Germany
	10:10 – 10:40 **COFFEE BREAK**	
ORAL PRESENTATIONS		**Chair: Jordi Esquena**
10:40 **11:00**	**Formulation of colloidal dispersions in ionic liquids for high temperature applications (OC 23)**	**Emmanuelle Dubois** Sorbonne University, Paris, France
11:00 **11:20**	**Synthesis of gold nanoparticles in microemulsion and nano-emulsion systems using aqueous leaf extract of C. chayamansa as reducing agent (OC 24)**	**Rocio Paola Carillo-Gaytan** University of Guanajuato, Cerro de la Venada S/N, Pueblito de Rocha, Guanajuato, Mexico
11:25 **11:45**	**New Generation Sustainable Polymers, Networks and Composites (OC 25)**	**Baris Kumru** Faculty of Aerospace Engineering, Delft University of Technology, The Netherlands
11:45 **12:05**	**Formulating nematic “tissues” of weakly bound discotic aggregates of carboxylate extended surfactants (OC 26)**	**Thomas Zemb** Institut de Chimie séparative de Marcoule, ICSM, France
KEYNOTE		**Chair: Jordi Esquena Moret**
12:15 **12:45**	**Challenge to incorporate bio-oil into sustainable marine fuels by direct mixture with fossil fractions (K04)**	**Barbara Heyberger** **TotalEnergies Research Center Solaize, France**
	12:45 – 14:00 **LUNCH**	
SUCCESS STORY		**Chair: Roland Ramsch**
14:00 **14:30**	**From cardanol to biobased polymers: a journey from lab to industry**	**Sylvain Caillol** Research Director CNRS Montpellier, France
ORAL PRESENTATIONS		**Chair: Roland Ramsch**

14:30 **14:50**	**Valorization of lignins as sustainable multifunctional ingredients for cosmetic formulations (OC 27)**	**Caroline Hadjiefstathiou** University Le Havre Normandie IFF-Lucas Meyer Cosmetics AgroParisTech, INRAE Versailles, France
14:50 **15:10**	**Preparation of robust carbon monoliths derived from phenolic resin for CO_2 separation (OC 28)**	**José Mosquera** Université de Technologie de Compiègne, ESCOM, Compiègne, France
15:10 **15:30**	**Development of new lipopeptide green surfactants from silk sericin (OC 29)**	**Alla Nesterenko** Université de Technologie de Compiègne, ESCOM, Compiègne, France
15:30 **15:50**	**Formulating nanostructured soft particles from a technical-grade diglycerol surfactant (OC 30)**	**Carlos Rodriguez-Abreu** IQAC-CSIC, Barcelona, Spain
15:50 – 16:15 **COFFEE BREAK**		
16:15 **16:45**	**How Microbicidal efficacy of Chemical Disinfectant product are evaluated currently in European? What will be the next steps needed to adapt to new Sustainable challenges? General overview proposed (OC 31)**	**Sophie Loeffert-Frémiot** Laboratoire Anios-Ecolab Sainghin-en-Mélantois, France
KEYNOTES		**Chair: Roland Ramsch**
16:45 **17:15**	**Biostimulants, a new class of functional additives in Agro: formulation challenges and sustainability impact (K05)**	**Jean-Christophe Castaing** Solvay, Aubervilliers, France
17:15 **17:45**	**Suspension Concentrate crop protection formulation design and performance for low spray volume and UAS spray application (K06)**	**Malcolm A. Faers** Bayer AG, Formulation Technology, Monheim, Germany

THURSDAY 6th JULY

PLENARY LECTURE		**Chair: Christel Pierlot**
8:30 9:30	**Novel "Photoswitchable" Molecular Assemblies (PL 05)**	**Hideki Sakai** Faculty of Science and Technology, Tokyo University of Science, Japan
ORAL PRESENTATIONS		**Chair: Christel Pierlot**
9:30 9:50	**Hydrogels based on functional hyperbranched polyglycerols (OC 32)**	**Jean-François Stumbé** University of Haute Alsace, France
9:50 10:10	**Formulation of molecular hydro-organogels based on modified aminoacids. Effect of chemical structure on gelation kinetics and thermoreversibility (OC 33)**	**Alain Durand** University de Lorraine, Nancy, France
10:10 – 10:30 COFFEE BREAK		
10:30 10:50	**Formulation and characterization of thermosensitive Hydrogels based on Cellulose and Xyloglucan (OC 34)**	**Géraldine Rangel** Bia INRAE Nantes Institut des Molécules et Matériaux du Mans France
10:50 11:10	**Self-assembly behavior in systems containing alkyl imidodipropionate and glutamate diacetate (OC 35)**	**Josmary Velásquez** Nouryon Surface Chemistry Stenungsund Sweden Chalmers University of Technology Göteborg, Sweden
11:10 11:30	**Interactions at the interface of gelled-oil nanoparticles in water: from dispersions to colloidal hydrogels (OC 36)**	**Bérénice Duret** University Le Havre, Normandie Le Havre, France
11:30 11:50	**Science-based formulation via webapps (OC 37)**	**Sander Van Loon** VLCI, Amsterdam, Netherlands *Van Loon Chemical Innovations B.V.*
KEYNOTE		**Chair: Christel Pierlot**
11:50 12:20	**Choosing the Right Method to Measure Accurately the Optimum Formulation in SOW Systems: Comparison and Specific Applications (K07)**	**Ronald Marquez and Jesús F. Ontiveros** University of Lille, UCCS, Lille, France North Carolina State University, Raleigh, USA
12:20 – 13:30 LUNCH		
SUCCESS STORY		**Chair: Jesus Fermin Ontiveros**
13:30 14:00	**The chemistry of tomorrow after the ecological transition, make way for new models**	**Olivier Choulet** Ecoat, Lyon, France
ORAL PRESENTATIONS		**Chair: Jesus Fermin Ontiveros**
14:00 14:20	**NMR relaxometry: a tool to probe complex formulations (OC 38)**	**Guillaume Mériguet** *Sorbonne University, Paris, France*
14:20 14:40	**NMR kinetic monitoring of the cutting fluid organic waste's hydrolysis all along the immobilization in**	**Christel Pierlot** University of Lille, France

	alkali-activated materials (OC 39)	
14:40 15:00	**Natural gums in complex formulations: molecular characterization by mass spectrometry (OC 40)**	**Christian Rolando** University of Lille, France Lesaffre International, France
15:00 15:20	**Numerical prediction of long-term stability of liquid formulations determined by visual observation and Static Multiple Light Scattering (OC 41)**	**Guillaume Lemahieu** Formulaction, Toulouse, France
15:20 15:40	**Thermal profiling with DWS to accelerate development from raw materials to finished (OC 42)**	**Roland Ramsch** Formulaction, Toulouse, France
15:40 16:00	**Advanced Dynamic Light Scattering and its Applications to Life Sciences (OC 43)**	**Coline Bretz** LS Instruments AG, Switzerland
16:00 16:20	**Meeting the challenge of better understanding the interfacial behavior of ingredients (OC 44)**	**Jean-Luc Bridot, Peggy Lechevalier,** TECLIS Scientific, France
16:20 – 16:40 COFFEE BREAK		
16:40 17:00	**Awards Ceremony and Conference closing**	

PLENARY LECTURES

Odile SONNEVILLE-AUBRUN is Head of Skincare, Make-up & Hair Physical-Chemistry Laboratories at L'Oréal. She was graduated from ESPCI (Ecole Supérieure de Physique et de Chimie Industrielle de la ville de Paris) in 1993. She obtained a Post-Master degree specialization in Soft Matter from Sorbonne University in 1994 and her PhD in Physical-Chemistry on biliquid foams from Sorbonne University in 1997. She has been working for L'Oréal Research for 25 years in the field of skincare, body hygiene, make-up & hair products innovation. Many of these innovations have been patented. Since 2016, she has joined L'Oréal College of Experts and has contributed to internal trainings in Physical-Chemistry applied to cosmetics. Her main research is focused on deep understanding of structure and properties of products from bulk to deposit on skin and hair and on formulation triggers exploration to deliver new products with high measured and perceived performance. This knowledge of applied Physical-chemistry makes it possible to identify and understand the major breakthrough innovations launched by L'Oréal.

Science driven formulation for sustainable & desirable cosmetic products

Odile Sonneville-Aubrun, PhD

Over the last ten years, the cosmetic industry has undertaken an in-depth transformation to propose innovating and desirable products yet being able to reduce its environmental impact across its entire value chain. This transformation has changed the way we design and make our products with sustainability as a fundamental requirement, and still strengthening our commitments for the coming years.

Rigorous scientific approaches and knowledge of our products remain a cornerstone of this shift towards even more sustainable & desirable products.

As a matter of fact, the qualification of our ingredients on key criteria such as origin (biobased, abundancy, circularity), transformation processes… with quantitative indicators is needed to guide formulators, to fix ambitious sustainability targets and to measure our progress. Furthermore, the systematic characterization of our ingredients based on physical and chemical parameters related to application properties and our ability to model them are major assets to realize this green shift for innovative & performing products.

Besides these two aspects, our success relies on a deep understanding of major cosmetic functions such as long lastingness, optical effects, care, sensory… as well as our capacity to control them through the right assembly of ingredients from bulk to deposit.

Finally, the reduction of water consumption upon products usage as well as scientific discoveries on skin and hair raises new formulation challenges to tackle to prepare the future of cosmetics.

Professor Slavka Tholakova obtained her PhD in Physical Chemistry at Sofia University in 2004 after a MSc in Chemical Physics and Theoretical Chemistry. From 2013, she is Professor at the Faculty of Chemistry and Pharmacy of Sofia University. She is head of the Department of Chemical and Pharmaceutical Engineering Faculty of Chemistry and Pharmacy Sofia University « St. Kliment Ohridski » from 2015. She is project leader of the research project "Natural bioactive substances for personal care products, cosmetics and dietary supplements", Centre of Competence "Sustainable utilization of bio resources and waste of medicinal and aromatic plants for innovative bioactive products", she is head of the Laboratory of "Formation and characterization of foams, emulsions and porous materials" in Centre of Excellence "National Centre for Mechatronics and Clean Technologies". She is the authors of 121 scientific papers, incl. Nature (1), Nature Phys. (1), Nature Comm. (1), Adv. Colloid Interface Sci. (5), J. Colloid Interface Sci (7), Langmuir (37), Colloids Surfaces A (17) cited > 4000 times, h-index = 36 (Scopus), 10 patents – 6 international (WIPO, US, Europe), 1 German, 1 French, 1 Japanese, 1 Chinese, 105 lectures and posters presented at International conferences and symposia (18 plenary or keynote). She has 14 completed PhD theses and 6 others under preparation. From 2004, she is the PI of 56 projects funded by international companies, incl. Unilever, BASF, Saint Gobain, Wacker, Lubrizol, Productalysa. From 2019 to 2021, she was the Leader of the Bulgarian team, ERC project (CoolNanoDrop No 841827, in collaboration with Queen Mary University of London), in 2017-2018, the Leader of the Bulgarian team, ERC project (ShipShape No 766656, in collaboration with Queen Mary University of London).

Plenary Lecture PL02

Physicochemical control of foam and emulsion properties

Slavka Tcholakova, Nikolai Denkov
Faculty of Chemistry & Pharmacy, Sofia University, Bulgaria
sc@dce.unisofia.bg

This presentation summarizes our recent understanding on how various essential foam and emulsion properties could be modified using appropriate conventional and natural surfactants, cosurfactants, polymers, solid particles and their mixtures [1-10]. On the basis of numerous experimental studies, we will discuss the effects of these substances on: (1) mean bubble and drop size upon foaming and emulsification; (2) foam and emulsion stability against coalescence and Ostwald ripening; and (3) foam and emulsion rheological properties. The observed experimental trends are analysed using existing and original theoretical models, and the key mechanisms and factors controlling these foam/emulsion properties are clarified. The interplay between the properties of the adsorption layers, the behaviour of the respective foam and emulsion films, and the hydrodynamic conditions during foaming and emulsification will be also discussed.

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6. Role of Interfacial Elasticity for the Rheological Properties of Saponin-stabilized Emulsions. S. Tsibranska, S. Tcholakova, K. Golemanov, N. Denkov, E. Pelan, S. Stoyanov, J. Colloid Interface Sci. 564 (2020) 264.
7. Origin of the extremely high elasticity of bulk emulsions, stabilized by Yucca Schidigera saponins. S. Tsibranska, S. Tcholakova, K. Golemanov, N. Denkov, L. Arnaudov, E. Pelan, S. Stoyanov, Food Chem. 316 (2020) 126365;
8. Physicochemical Control of Foam Properties. N. Denkov, S. Tcholakova, N. Politova-Brinkova, Curr. Opin. Colloid Interface Sci. 50 (2020) 101376.
9. Surface Phase Transitions in Foams and Emulsions. N. Denkov, S. Tcholakova, D. Cholakova, Curr. Opin. Colloid Interface Sci. 44 (2019) 32–42
10. Control of Ostwald Ripening by Using Surfactants with High Surface Modulus. S. Tcholakova, Z. Mitrinova, K. Golemanov, N. Denkov, M. Vethamuthu, K. P. Ananthapadmanabhan, *Langmuir*, 27 (2011) 14807.

Funding: Part of these studies was supported by Operational Program “Science and Education for Smart Growth” 2014–2020, co-financed by European Union through the European Structural and Investment Funds, Grant BG05M2OP001- 1.002-0012 “Sustainable utilization of bio-resources and waste of medicinal and aromatic plants for innovative bioactive products”.

Plenary Lecture PL03

Prof. Andreas Klamt studied Physics at the University of Göttingen, Germany, and gained his Ph.D. in Theoretical Solid State Physics at the Max-Planck-Institute and the University of Stuttgart, in 1987. He joined Bayer AG in 1987, learned Computational Chemistry on the job, and was promoted to the Head of the Computational Chemistry Department in 1996. He left Bayer in 1999 to found COSMOlogic which is now part of Dassault Systèmes where he is Senior Scientific fellow. In 2005, he obtained his Habilitation in Physical and Theoretical Chemistry from the University of Regensburg where he currently holds the position of honorary professor.

Prof. Klamt is a pioneer in the prediction and quantification of solvation effects. As his first major achievement he invented the Conductor-like Screening Model COSMO, which is widely used in quantum chemistry for the quantification of solvation effects. He is the creator of the COSMO-RS method which combines a quantum chemical treatment of solutes and solvents with a fast and effective statistical thermodynamics procedure for the molecular surface interactions. His method enables the calculation of thermophysical data for liquid systems without any prior experiments. In recent years he has considerably extended the field of application of his method by developing new tools (COSMOplex and COSMOquick) which allows to predict the properties of relevant systems in formulation science such as micelles, ionic liquids, deep eutectic solvents, polymers and complex materials.

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https://www.linkedin.com/in/andreas-klamt-75534046/
https://research.com/u/andreas-klamt

Applications of the COSMO-RS and COSMOplex methods in formulation science

Prof. Andreas Klamt

The COSMO-RS method is as highly efficient shortcut connecting quantum chemical information about the molecular polarity directly with macroscopic thermodynamic properties as solubility, partition coefficients, activity coefficients, or vapor pressures of a wide range of organic molecules in pure or mixed solvents. By that, COSMO-RS strongly increases the chemical “formulation space”, because new or even virtual molecules can be included in a screening for optimal formulations, for which the data would be missing otherwise. The COSMOquick tool even allows slightly less accurate, but very fast property predictions, avoiding the quantum chemical calculations, and thus it enables screening of almost unlimited virtual chemical spaces as solutes, solvents and additives.

In the recent years we succeeded to extend the COSMO-RS method to inhomogeneous liquids. This extension is named COSMOplex, because it enables the simulation of complex liquid systems as interfaces, surfaces, micelles and even micro-emulsions. A few applications of this exciting tool will be presented.

Prof. Kunz is head of the chair of physical chemistry II at the University of Regensburg in Germany. His group is specialised in solution chemistry (complex liquids, their structures, and interfaces) and in green chemistry. The activities span from very fundamental research to applied and industrial chemistry with a special focus on product formulation. He is also owner of a company, the SKH GmbH, which develops new formulations for various small, medium sized, but also big international companies. Here the focus is on cosmetics, perfumes, cleaning agents and plant extraction.
At present, **Prof. Kunz** authored or co-authored 330 peer-reviewed publications, further to several patents, book chapters, book editions etc. Kunz' h-index is 56 (Web of Science) and 67 (Google Scholar), his papers are currently cited more than 12.400 times (>17.000 according to Google Scholar). For his basic and applied research, he received several prizes, e.g., the Rhodia prize from the European Colloidal Society, the Gay-Lussac prize from the French government and the Steinkoff prize from the German Colloidal Society.

For more information, see : Research Group Prof. Werner KUNZ – Universität Regensburg (uni-regensburg.de)

Plenary Lecture PL04

Green High Performance Solvents and Related Formulations

Werner Kunz
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The proper choice of solvents is crucial for high performance formulations. In parallel, the quest for green liquids is more and more noticeable in many industrial sectors. However, further to marketing advantages, there is a strong need to identify solvents that are not only “greener”, but also competitive, if not better in terms of price, availability and performance.

In the present contribution, I will discuss some of these liquids that are currently still neglected or not yet widely used, but that have a significant potential for future applications. For example, gamma-valerolactone (GVL) shows very promising properties such as a very high solubility, e.g., for several polymers, together with a very low ecotoxicity, excellent biodegradability, and a complete miscibility with water [1]. Whereas the price is currently still prohibitive, this will change next year, when a new industrial plant in Germany will start its large-scale production.

Whenever food and cosmetic formulations with natural products are required, there is a particular need to carefully choose adequate solvents. Thanks mainly to Prof. Farid Chemat’s efforts, the bio-based solvent 2-methyltetrahydrofuran (MeTHF) has finally been recognized this year by the European Union as allowed food extractant and a valuable alternative to hexane [2]. We also propose alternative solvents, for example and among others (NADES) triacetine (E 1518) that can be made miscible with water by adding an appropriate amount of ethanol [3].

Finally, I will talk about an interesting class of natural hydrotropes, i.e., polyphenols and related antioxidants. Not only can they stabilise classical formulations against oxidation, but, in addition, they can help significantly increase the solubility of very hydrophobic substances in the “greenest” of all solvents, which is water [4].

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Professor Hideki Sakai graduated from the University of Tokyo in 1990 and got master degree (1992) and Ph.D. (1995) in Applied Chemistry from the same university under the supervision of Prof. Akira Fujishima. After receiving his PhD degree, he took the position in Faculty of Science and Technology, Tokyo University of Science (TUS) as an assistant professor (Prof. Masahiko Abe's group). He collaborated with Prof. Eric W. Kaler of University of Delaware (U.S.A.) as a visiting scientist from 1998 to 1999. Currently he is a professor and chair of Division for Colloid and Interface Science, TUS. His research interests include molecular assembly formation of amphiphilic molecules (vesicle, micelle, worm-like micelle), photo- and electro-responsive surfactants, and also preparation of nanostructured materials using interfacial chemical techniques. He is a vice dean of Division of Colloid and Interface Chemistry, Chemical Society of Japan since 2019.

Novel "Photoswitchable" Molecular Assemblies

Hideki Sakai
Faculty of Science and Technology, Tokyo University of Science, Japan

Surfactant molecular assemblies that form, collapse, or change morphology upon application of external stimuli, such as light irradiation, redox reaction, and pH, have been studied extensively with a view to applying for controlled release of drugs and perfumes encapsulated in the assemblies. Our particular interest lies in active control of interfacial properties and molecular assembly formations by means of photo-responsive surfactants. The benefits of photo-responsive nature as an external stimulus over other stimuli include scalable miniaturization and limited chemical contamination, allowing for the development of green sustainable systems. In this presentation, I would like to address some of our recent studies regarding formation control of molecular assembly using novel "photo-switchable" surfactants. First, I will introduce photo-cleavable surfactants modified with cinnamic acid derivative which can be decomposed by UV light irradiation to decrease interfacial chemical properties. I will also present novel amphiphilic lophine dimers showing rapid change in interfacial chemical properties by light irradiation.

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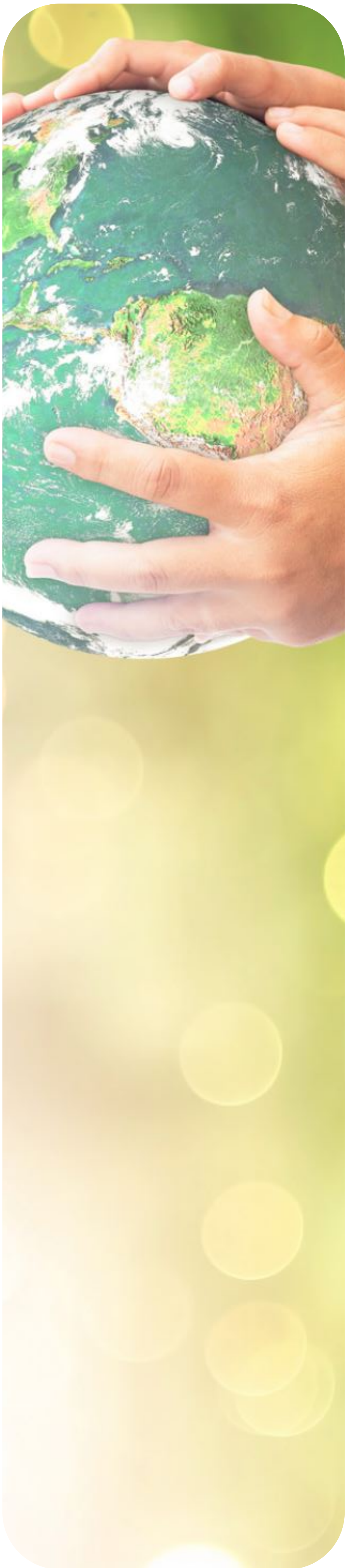
KEYNOTES



Dr Tim J Wooster is a colloids and polymer scientist focusing on the biophysics of emulsions, foams and particles. He has been working at Nestlé Research Lausanne for the past 12 years, where he is a Dispersions Expert within the Institute of Materials Science. Fascinated by colloids science he is passionate about the formulation challenges associated with dairy and plant based liquid products. A leading international reputation in food emulsion science, he has published over 56 publications (H-Index 32, >4900 citations) in leading colloid, polymer and interface science journals. At Nestlé he has a lead role in developing scientific understanding enabling the formulation of stable, nutritious, and more sustainable emulsion & foam-based products.

Sustainable, Nutritious, Plant based and/or Dairy? How Nestlé is addressing its future formulation challenges using advanced & traditional approaches

Nestlé's work is guided by a desire to contribute to nutritious and sustainable diets, to help protect, renew and restore natural resources. In fulfilling this our product developers consider the nutrition, sustainability, economic and most importantly taste and texture of the products they are formulating. The emergence of legume/cereal plant proteins as alternatives to dairy proteins provides a particular challenge of ensuring functionality whilst having an appealing taste. In my presentation I will highlight how Nestlé is using a combination of advanced and traditional approaches to meet these challenges. The formulation of an RTD beverage will be used to highlight the different scientific challenges that arise along an RTDs development lifecycle. This presentation will cover aspects ranging from the plant vs dairy protein science, emulsion formation and thermal stability, foam creation and drainage and finally aspects of stability in use

Dr. Anne-Laure Fameau studied Food Science before coming to soft matter during her thesis. She received her Ph.D. in Physical Chemistry from the University of Nantes in 2011. During her Ph.D, she worked at the Laboratory Léon Brillouin at CEA Saclay (French Neutron Center) as well as the French National Institute of Agricultural & Environment Research (INRAE) in Nantes. At the end of 2011, she obtained a researcher position at INRAE in Nantes. In 2015, she joined L'Oréal company in the Physical-Chemistry Department in Paris. In 2018, she received the European Young Lipid Scientist Award and the Langmuir Prize at ECIS Conference. In 2021, she received the AOCS Young Scientist award. She came back to academia at INRAE in October 2021. Her research interests are in the field of responsive soft materials based on lipids and green surfactants with a particular emphasis on foams and interfaces. Her research is focused on the development of these systems and their detailed structural characterization using scattering techniques such as SAXS and SANS. In the past few years, she is also focusing on oil foams based on vegetable oils and lipid components for Food and Cosmetic applications. All of her work resulted in 36 scientific papers, 12 review articles, 5 book chapters, and 19 patents. **Dr. Fameau** also enjoys transmitting her passion for science to young students. She visited many schools and gave scientific talks to students to promote science in France, and especially to promote science for girls.

Keynote K02

Non-aqueous foams stabilized by crystalline particles: from design to applications

Dr. Anne-Laure Fameau

Liquid foams are complex colloidal systems based on gas bubbles dispersed in a liquid continuous phase [1].Two different categories of liquid foams exist: aqueous or non-aqueous. In contrary to aqueous foams, which have been extensively studied, non-aqueous foams represent a new promising emerging field [1]. Two types of non-aqueous foams are gaining interest: oil foams based on vegetable oil (oleofoams) and alcohol-based foams [2,3]. Oleofoams are a promising option to develop new food products combining both a reduced fat content and new appealing textures and sensorial properties. Oleofoams also possess other advantages of interest for cosmetic and pharmaceutical applications: long-term stability lasts for months even above room temperature, reduction in microbial spoilage as water is absent and so preservatives are not needed [4]. Therefore, oleofoams appear to be a perfect new product regarding the increasing trend to develop "clean label" products in various industries. Alcohol-based foams are gaining interest nowadays since the global pandemic due to COVID-19 and the frequent use of alcohol-based hand sanitizers as recommended by the World Health Organization.

The main difference between aqueous and non-aqueous foams comes from the relatively large difference in the surface tension of the solvents [1]. For non-aqueous systems, the low surface tension makes the adsorption of hydrocarbon-based surfactants energetically unfavourable. One way to produce and stabilize non-aqueous foams is to use surfactant crystalline particles, which can adsorb at the air-liquid surface [5]. In this talk, we will present how crystalline particles based on fatty acids and fatty alcohols can lead to the production and stabilization of both oleofoams and alcohol-based foams [2,6]. The formation and stabilization mechanisms of these two types of non-aqueous foams are the same and based on the adsorption of crystalline particles at the air-liquid surface, which reduce the bare surface area by their presence rather than lowering the surface tension [5]. The key parameter for crystals to adsorb at the air-nonaqueous liquid surface is to exhibit a suitable three-phase contact angle below 90°. These foams are ultrastable due to the dense layer of adsorbed crystals at bubble surfaces that considerably reduce both disproportionation and coalescence.

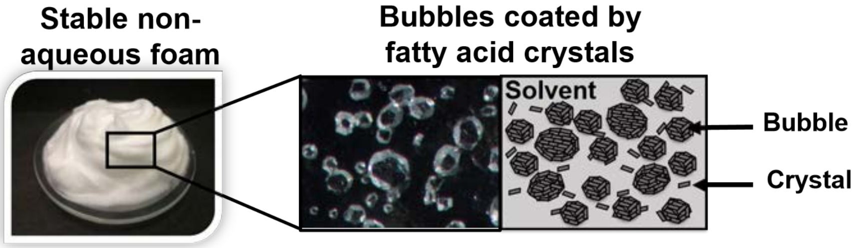


Illustration of non-aqueous foam stabilized by the presence of fatty acid crystals both in bulk and at the interface as observed by polarized light microscopy

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Frank Runge studied Chemistry at the University of Cologne, Germany, and received his PhD in Physical Chemistry of microemulsions in 1992. This was followed by a Postdoc in Physical and Polymer Chemistry at the University of Wisconsin-Madison, USA, working on polymer monolayers. In 1994, he joined BASF's Polymer Research Division and worked on formulation and colloid chemistry aspects for various industrial (paper chemistry, home and personal care, coatings, resins) and life science (agricultural, nutrition and pharmaceutical) applications. Afterwards he moved to the BASF operating division Nutrition & Health and later to Agricultural Solutions working in different functions in R&D, Marketing and Operations, fostering his scientific and technical-economical experience in formulation. From his managerial assignments including a 6 year stay in Brazil he gained experience in leading international teams (Europe, USA, Brazil, Japan). Returning to Germany in 2015, he headed the Global Formulation Research Platform within BASF's Central Research with laboratories in Germany, USA and China, collaborating with all BASF operating divisions that are active in formulation. In 2022, he took over the BASF Research Program Lead Advanced Formulation including Corporate Research and Operational Development project groups

Advanced Formulation from an industry perspective – trends and new strategies, methods, and tools to scope with new challenges

Frank Runge

Formulation is an important area for BASF's business success - more than 60 % of its sales are based on formulations and materials that our customers are using in their formulations. Similar statements can be made for the whole industry active in the downstream area.

The 'traditional' product driven formulation developments are based on experience and empirical knowledge with strong focus on applications. To successfully manage current and future challenges, 'advanced' formulation development is needed. That includes fundamental scientific formulation understanding, high throughput technology, lab automation and data management as well as modern *in-silico* methods, e.g., with the use of supercomputers. These approaches are heading towards the prediction of formulation and application performance in complex, multi-component systems.

On top, supporting the industry transformation towards a more sustainable future is the overarching challenge in formulation with the highest innovation demand we are facing nowadays. Sustainability aspects include e.g., biodegradable and/or biobased formulations, substitution of regulatory or environmentally unfavored formulation ingredients as well as improved formulants and formulation processes for low energy consumption. Formulation concepts can also contribute to understand and resolve Circular Economy challenges e.g., in mechanical recycling of materials.

In addition to sustainability the other main challenges in formulation are stability and performance of chemical and biological ingredients in formulation, innovation needs for new technology concepts, speed-up time-to-market and cost competitiveness.

In this keynote an overview and examples from industry perspective are given that demonstrate the path forward in Advanced Formulation.

Barbara Heyberger holds a PhD from the National Polytechnic Institute of Lorraine obtained in 2002. She is working for TotalEnergies since 2002 on heavy fuel oil and spent the first ten years at Solaize Research Center (France) trying to reduce pollutants emissions from boilers and refining furnaces using additives or urea injection. In 2009, she joined the ISO experts working group in charge of the marine fuel specifications and the CIMAC (International Council on Combustion Engines) working group dedicated to Fuels. In both WGs she is leading the sub-group dedicated to marine fuel stability. She has also the chair of the marine fuel special task force at Concawe. She contributes to CIMAC guidelines and Concawe Technical Reports related to marine fuels properties including safety, stability, bio marine fuels formulation…

In 2013 she moved to TRTG (TotalEnergies Research & Technology Gonfreville) where she is in charge of the marine fuel laboratory at OneTech, Technical Lines, Process department and recognized as marine fuel specialist. The marine fuel laboratory is working on the evaluation of sustainable bases that will help to achieve the decarbonization targets of the shipping industry.

Challenge to incorporate bio-oil into sustainable marine fuels by direct mixture with fossil fractions.

Barbara Heyberger

The market of Sustainable Marine Fuels (SMF) is continuously growing and need to be adapted to renewable fuels and guarantee net-zero GHG emissions and a circular economy by 2050. One of the most appropriate ways to help the energy transition at short and middle terms in marine transport is the use of biofuels come from bio-based waste. Pyrolysis and HTL technologies allow to transform the organic waste like agricultural or forestry residues and bio-wastes in bio-based oil fractions which are a high potential to produce SMF. In the case of bio-oil produce by pyrolysis, the challenges for its partial incorporation into fossil mixtures are associate to high number of oxygenated compounds which makes its physicalchemical properties incompatibles with a heavy fossil fuel and makes it difficult to accomplish the current regulatory requirements.

Jean-Christophe Castaing *(Solvay, Research and Innovation, Center of Paris)* is Open Innovation Director at Solvay Novecare. He graduated from Ecole Centrale (Paris) and holds a PhD in Physical chemistry and materials Science from Univ. P&M Curie (Paris). Since he is working in industry, his research focus has been in the field of complex water borne formulations, bridging the design of individual components with the functionalities expected in markets such as coated paper, paints, home and personal care and agro-chemistry. He held several project leader or managerial positions in R&D within Solvay, striving to build links with research in Academia (he was the Director of a CNRS-Solvay joint lab, and coordinator of an EU project). He is a Solvay Research Fellow

Biostimulants, a new class of functional additives in Agro : formulation challenges and sustainability impact

C. Vernay, A Wathelet, JC Castaing

The general trend in the agrochemical industry is to minimize off-target impact of active ingredients presenting possibly toxicity or ecotoxicity issues. This has favored the emergence of a new class of inputs, called biostimulants, that help the plants fight biotic or abiotic stresses, reducing the need for “classical” active pesticides.

The use of those new inputs, which can be foliar, soil or seed applied, comes with a number of challenges. Formulation is the first problem to solve. Biostimulants are not usually as “active” as phytopharmaceutical molecules, their use rate can be slightly larger: this has to be managed to be compatible with existing formulations and application tools. A second challenge is to make the proof of their efficacy, as their effect on plant metabolism is most of the time less specific as traditional pesticide treatments. Then, a last challenge is to demonstrate the real environmental benefit of using a biostimulant.

We present here a case study focusing on a biosourced seed applied biostimulant. We review first the specific compatibility and application criteria that the formulation has to fulfill to be used in existing seed treatment plants. We then show the result of multiyear field trials campaigns, comparing the yield of crops such as corn, soybean, rapeseed and sunflower grown in the presence and absence of the biostimulant, considering also conditions of water or nutrient shortage. We conclude with a detailed life cycle analysis to quantify the environmental impact of a biostimulant.

Keynote K06

Suspension Concentrate crop protection formulation design and performance for low spray volume and UAS spray application

Malcolm A. Faers
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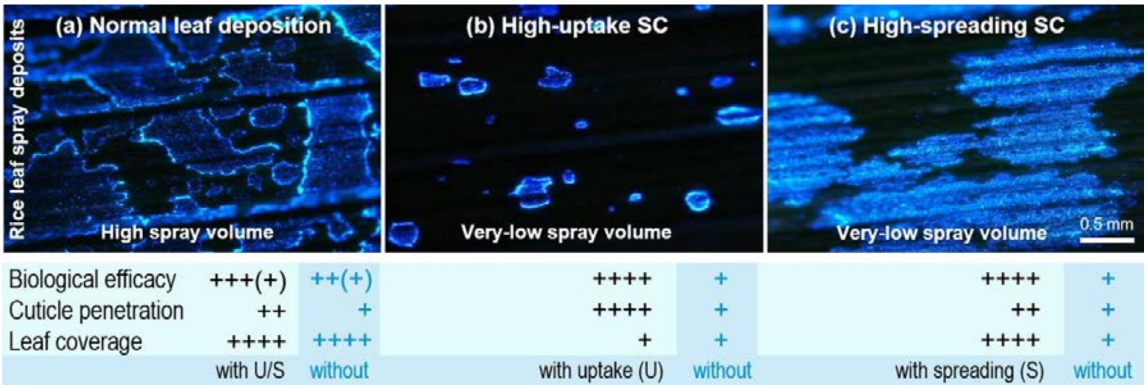
Designing crop protection formulations is a complex challenge, the final product must fulfil several different criteria such as performance, innovation, differentiation, safety, be registerable, cost, sustainability, stability and be robust for manufacture for example. These criteria often compete against each other during formulation design and finding effective solutions in the design space is complex. This raises the question of how can solutions be found efficiently? The number of recipe components, process variations and product criteria make it highly unlikely that solutions will be found that could be foreseen. Colloid and interface science are valuable tools here in the formulation design process to better understand the large and complex design variable space.

Recently, unmanned aerial systems (UAS) or drones have emerged (rapidly in APAC) as alternative and potentially disruptive methods to apply products more sustainably with the opportunity to reduce the CO_2 footprint of spray application but with the consequence of limited carrying capacity for the spray liquid (~10-30L), resulting in spray volumes down to ~8-30 L/ha (from ~100-1000 L/ha). At these very-low spray volumes, the low number of spray droplets (typically VMD 100 to 250 microns) impacts the deposition and coverage, which can result in reduced efficacy. This creates interesting opportunities for formulation design where the higher concentration of surfactants and other formulants in the spray droplets can be utilised to enhance wetting, spreading and biodelivery of active ingredients to the target.

At very-low spray volumes, SC formulations containing relatively low dose rates (g/ha) of formulants (adjuvants) that enhance spreading on the leaf surface, including organosilicone based surfactants, can maintain good spreading on leaf surfaces containing epicuticular wax crystals. In associated experiments, SC formulations containing certain nonionic surfactants showed enhance uptake at very-low spray volumes through the presence of coffee ring spray deposit microstructures. Both demonstrated enhanced biological efficacy in the greenhouse.

These formulations overcame the biodelivery limitations of reference SC formulations without these formulants, offering improved sustainability opportunities. Furthermore, this result is unexpected and surprising when the low dose rate of formulants (adjuvants) used (g/ha) is considered. It is also interesting how important the distribution of active ingredient(s) and adjuvants on the leaf surface is for product performance.



	with U/S	without	with uptake (U)	without	with spreading (S)	without
Biological efficacy	+++(+)	++(+)	++++	+	++++	+
Cuticle penetration	++	+	++++	+	++	+
Leaf coverage	++++	++++	+	+	++++	+

Fig 1. Foliar spray deposits on rice plants illustrating different deposit structures (coffee rings/uniform) and distributions for high (a) and very-low spray volumes with uptake promoting (b) and high spreading surfactants (c).

Ronald Márquez holds a Chemical Engineering degree and a Ph.D. in Applied Sciences from Universidad de Los Andes (ULA), Venezuela. He is currently a Postdoctoral researcher at ESPCI-Paris and TotalEnergies, and a visiting scholar at the University of Lille, France. His research focuses on the compatibility of wood pyrolysis oils with petroleum-derived fuels, with one patent in the application process. In 2020-2021, he was a Postdoctoral Fellow at the Department of Forest Biomaterials at NC State University. In 2019-2020, he served as Associate Professor and Head of Department of the Chemical Engineering School at ULA. His research has been primarily focused on upcycling biobased materials to value-added products, physicochemical formulation of surfactant-oil-water systems, and emulsion stability, including their characterization through interfacial rheology and surface science techniques. He has won the prize for the Best original paper of the Journal of Surfactants and Detergents (JSD) in both 2019 and 2023, which was awarded by the American Oil Chemists' Society (AOCS) and the American Cleaning Institute. He is an Associate Editor of the JSD and a Guest Editor in Frontiers in Chemical Engineering. He has an H-index of 10 and over 300 citations according to Scopus.

Jesus Fermin Ontiveros is an Associate Professor at the Ecole Nationale Supérieure de Chimie de Lille (ENSCL-Centrale Lille Institute). He graduated as an engineer in Mérida-Venezuela, where he started his research on separation processes using surfactants in the Formulation Interfaces Rheology and Processes (FIRP) laboratory directed by Jean Louis Salager. He obtained his PhD in 2014 at the University of Lille focused on the Classification of biocompatible surfactants and oils by measuring the Phase Inversion Temperature and comparing equilibrium phase diagrams. In 2015, he joined the Colloid Catalysis and Oxidation team (CISCO-UCCS) in which he developed a research activity related to the formulation of emulsions and microemulsions, using in particular the phase inversion process to characterize the hydrophilic-lipophilic balance of surfactants but also for industrial applications such as enhanced oil recovery or emulsification of viscous oils. He has published 32 papers and 2 patents and has co-supervised 4 PhD students.

Choosing the Right Method to Measure Accurately the Optimum Formulation in SOW Systems: Comparison and Specific Applications

Ronald Marquez[1], Jesús F. Ontiveros[2*] and Jean Louis Salager[3]*
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Optimum formulation is defined as the physicochemical condition at which a Surfactant/Oil/Water system at equilibrium presents a minimal interfacial tension, and the surfactant has the same affinity for both oil and water. The search for the optimum formulation of SOW systems is critical for diverse industrial applications, ranging from pharmaceuticals to cosmetics to oil recovery. Indeed, knowing this condition allows to formulate stable emulsions by working at a certain distance. The incorporation into products of new, sustainable, and safer surfactants, such as biobased ones, can pose a significant challenge due to their intricate composition and unique properties, and the precise determination of the optimum formulation is essential to characterize them accurately.

We present a systematic approach to determine the optimum formulation of SOW systems using a variety of techniques, including conventional ones such as phase behavior, minimum interfacial tension, emulsion stability, electrical conductivity and viscosity. We also explore innovative techniques such as minimum dilational modulus (OSDIR), nuclear magnetic resonance (NMR), X-ray microcomputed tomography (Micro CT), small-angle X-ray scattering (SAXS), differential scanning calorimetry (DSC), dynamic light scattering (DLS), light backscattering (LBS), near-infrared spectroscopy (NIR), and differential dielectric sensors (DDS) [1]. We discuss challenges that can arise when determining the optimum formulation, such as hysteresis and liquid crystal formation. By considering these factors and selecting the most suitable technique based on the specific application, formulators can effectively incorporate new surfactants into their formulations to achieve best performance.

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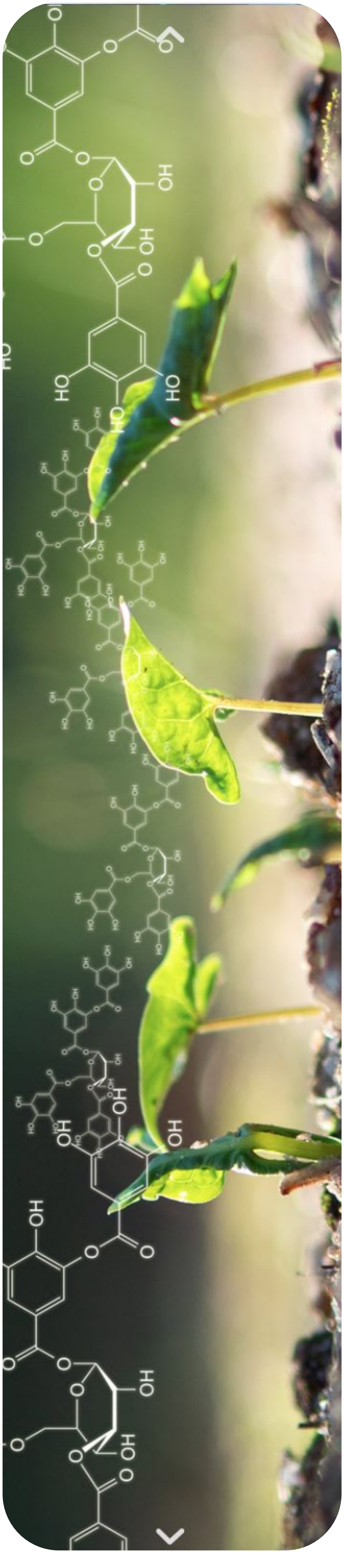
SUCCESS STORIES



Sylvain Caillol is Research Director at CNRS. He graduated engineer from the National Graduate School of Chemistry of Montpellier in 1998 and then received his M. Sc. Degree in Chemistry from the University of Montpellier. He received his PhD degree in 2001 from the University of Bordeaux. Subsequently he joined Rhodia Company where he headed the Polymer Research Department in the Research Center of Paris. In 2007 he joined the CNRS at the Institute Charles Gerhardt of the University of Montpellier where he started a new research topic dedicated to Green Chemistry and Biobased Polymers. He is co-author of more than 250 articles, patents and book chapters. He won the Green Materials Prize in 2018 and 2020 and he entered the World Top Scientist (Stanford) in 2021.

From cardanol to biobased polymers: a journey from lab to industry

Sylvain CAILLOL, PhD HDR Research Director CNRS, sylvain.caillol@enscm.fr

Recent years have witnessed an increasing demand on renewable resource-derived polymers owing to increasing environmental concern and restricted availability of petrochemical re-sources. Moreover, most of thermosetting materials contain aromatic monomers, able to confer high mechanical and thermal properties to the network. Therefore, the access to biobased, non-harmful, and available aromatic monomers is one of the main challenges of the years to come. Cardanol is a naturally occurring phenol, extracted from Cashew nutshell liquid, a non-edible byproduct of cashew agro-industry. We proposed a platform approach for the synthesis of various building blocks from cardanol in one or two-steps syntheses. Various routes were used for the synthesis of di- and poly-functional building blocks used thereafter in polymer syntheses. Epoxidation was used to obtain both polyepoxide networks, carbonation led to non-isocyanate polyurethanes. We designed cardanolbased flame-retardant alkyd resin or PVC Plasticizers. Various (meth)acrylate monomers we also synthesized for radical aqueous emulsion polymerization. These polymers have successfully used for industrial applications.

Olivier Choulet is the Chief executive officer of the Ecoat company which he created in 2011 as a start-up in biobased and eco-friendly polymers for the Coating industry. He was graduated from CPE-Lyon in 1993 and obtained a MBA in Business at the ESSEC Business School in 2002. He worked then at Rohm and Haas for 8 years as a global marketing manager, then at Dow for 4 years in Europe, USA and Asia in research, production, strategy and business management. He has skills in Materials Science, polyurethane, paint, International Business, and polymers. Ecoat (HQ in Grasse in France) is today a company which helps the Coatings industry to achieve its ecological transition.

The chemistry of tomorrow after the ecological transition, make way for new models!

ORAL COMMUNICATIONS

Accelerate the development of cosmetic ingredients thanks to sensory/*in vivo* correlated and predictive physicochemical characterizations

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Three years is an optimistic time frame for placing a new cosmetic ingredient on the market. From the initial idea to the market launch, the development of a high-performance biobased raw material can be a race against time. In particular, the iterations going on between the design and formulation departments in order to identify and optimize the best candidate can especially be time consuming.

The *in vitro* testing phase can be a real ally. Indeed, if a good performance test must permit the rapid quantification of a property while being discriminating, the real challenge is to succeed in predicting the consumer's perception. Such a tool allows the most relevant new structures to be identified quicker, even if they have not yet been fully evaluated toxicologically, and therefore cannot be screened by sensory analysis or *in vivo* testing. Identifying at the same time the determinant physicochemical parameters to establish structure-property relationships would lead, in an ultimate step, to synthesize a molecule knowing in advance its sensory impact.

To this end, we decided to integrate correlation trials during the development of our characterizations. Several levels of success were obtained: i) a "yes/no" correlation predictive of the water resistance of a cosmetic composition film; ii) a linear correlation predictive of the soaping effect of emulsifiers.

i) Water resistance (WR) is a claim particularly desired for sunscreen products. It is determined *in vivo* according to a normalized method published by Cosmetics Europe. While this test is essential for a product launch, it is costly and very time-consuming in the development phase of a new ingredient. The test developed here is based on the *in vivo* tests of Haggens *et al.*[1] and Marcel *et al.*[2] which evaluate WR by measuring a water contact angle on previously protected skin. Indeed the ability of water to wet the protected skin can reflect a water repulsion and therefore a WR above a certain angle. Work consisted of selecting a substrate and determining all the parameters required to transpose this test to *in vitro* conditions. Around thirty in-house formulas and twenty products from the market were simultaneously evaluated according to our protocol and a classical *in vitro* test with immersion. About fifteen products judiciously chosen according to their contact angle were then evaluated using a normalized external *in vivo* test. Although the complexity of the measurement did not permit a perfect correlation, it does allow the products to be classified into three categories according to the contact angle measured: WR/uncertain/not WR.

ii) The second study consisted of developing an *in vitro* test that reproduces the whitening effect characteristic of the soaping effect on a skin model, despite the large variability of the phenomenon depending on the individual, the product or the movement applied. Nevertheless, the data generated by our method correlated with data from a sensory analysis of 10 products carried out by 36 panelists, resulting in a coefficient of correlation R^2 of 0.93.

These two cases illustrate that this approach allows effective discrimination between in-house formulas while highlighting the impact of some structural fragments or specific ingredients. They also offer the advantage of limiting toxicological validation to the final candidate, of being fast (< 40 min), reproducible, precise, using very little product amount (< 1 mL) and inexpensive.

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Formulation and applicability of fully and homogeneous topical Pickering emulsions, and description of the phenomena that occurred within the system

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In the cosmetic industry and innovation, the interest in Pickering emulsions is growing in accordance with the increased will of customers to be responsible and respectful of the environment and sustainability. Thus, a reasonable choice of particle nontoxic and non-pollutant is a promising alternative to some problematic surfactants[1].

Fundamental research on Pickering emulsion focuses on colloidal system stable against coalescence but which doesn't fit with the demand of the industry to obtain a fully emulsified, stable against reversible phenomena (such as flocculation, sedimentation, and creaming)[2], and which resist variation of classical parameters and addition of essential components. In this study, a stable emulsion is defined by the capacity of the particle to anchor at the interface and stabilize an emulsion over time against coalescence, as well as against common reversible destabilization phenomena to obtain a homogeneous emulsion with the aspect of a commercial product[3]. In this work, we focus on a non-modified and nanosized clay particle.

Once this system is obtained, the second objective is to understand the organization of the system by studying the physicochemistry parameters responsible for the obtention of such emulsion. Then, to insure the applicability of stable colloidal dispersions several factors were modified, for example, the oil polarity and the pH, and other classical cosmetic ingredients were added. To understand the influence of each modification the emulsion properties will be described by several analytic methods (such as macroscopic and microscopic studies of the structure and rheology).

This promising particle reaches the desired system and is able to ensure the stability of the different conditions imposed on the emulsion, it is a valuable asset for the future of innovation in cosmetic formulation. The physicochemistry analysis permit understanding of all the phenomena which occur in these colloidal dispersions.

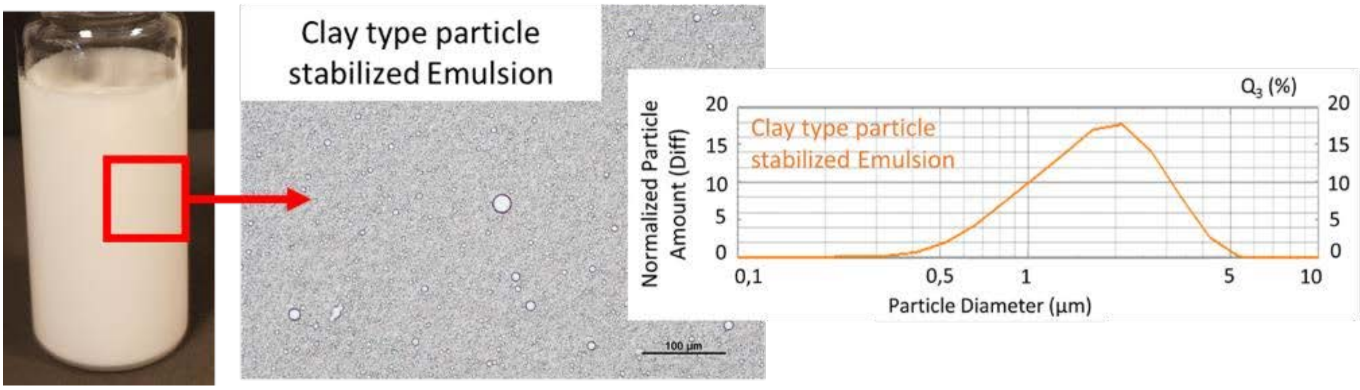

Fig 1. Macroscopic view of the fully emulsified emulsion and its microstructure

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Hybrid systems combining hyaluronic acid and liposomes for local drug delivery:
how liposome characteristics govern the microstructure and their release

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Liposomes play a leading role among nanomedicines due to their versatility and excellent safety profile. These biodegradable and deformable vesicles formed by phospholipid bilayers surrounding an aqueous core can encapsulate hydrophobic or hydrophilic molecules. Incorporating liposomes into concentrated polymer solutions or hydrogels is an efficient strategy to deliver drugs locally. It prevents the rapid elimination of the drugs and favors their prolonged residence time at the administration site and their controlled release for an extended duration. Mixtures of hyaluronic acid (HA) in the semi-dilute entangled regime, with liposomes at high lipid concentrations, showed a great interest in otology [1] and ophthalmology [2]. However, little is known about their microstructure and how the liposome characteristics influence their release from these hybrid systems. The aim of the study was to assess the influence of liposome surface (neutral, cationic, anionic, or anionic and covered with poly(ethylene glycol) (PEG)) and size. Several complementary methods were combined: small angle neutron scattering, cryogenic-electron microscopy, dynamic light scattering, rheology, and a Transwell® release model constituted of two compartments separated by a membrane.

Whatever the conditions probed, liposomes kept their integrity in HA. Entropic effects and the interactions between HA chains and liposomes drove the dispersion of liposomes within the polymer network. Indeed, when there were repulsions or no electrostatic interaction between HA and vesicles, a depletion mechanism led to the substantial aggregation of the liposomes. Anionic and PEGylated liposomes formed dense clusters with an amorphous organization, whereas cationic ones were more dispersed and formed less dense aggregates due to their complexation with polyanionic HA (Fig 1) [3]. Liposome characteristics also governed liposome release from the hybrid systems (Fig 1). At 150 nm, anionic liposomes covered or not by PEG chains migrated from the hybrid systems, whereas cationic and neutral ones did not. Furthermore, at 200 nm and above, the migration of PEGylated liposomes was strongly hindered. Below 200 nm, their release was faster when their size decreased. Multiple and complex mechanisms were involved including interactions between HA and liposomes, water exchanges, liposome migration, swelling and erosion, and HA reptation. Their relative importance over time depended on liposome characteristics.

The HA-liposomal hybrid systems appeared as a versatile formulation platform allowing different strategies for local drug delivery, with either immobilized liposomes acting as drug reservoirs or mobile liposomes released in the biological media and modifying drug distribution.

Water in Water novel systems for the encapsulation of active components

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Water-in-water (W/W) emulsions are liquid/liquid biphasic systems that consists of droplets of one aqueous solution, dispersed into another aqueous solution [1,2]. Both solutions contain water as the common solvent, and are in thermodynamic equilibrium because of the incompatibility between two hydrophilic solutes. W/W emulsions can be prepared without oil and without surfactant, and thus, they constitute biocompatible carriers for delivery of active components. The main problem in formulation of W/W emulsions is achieving a proper colloidal stability, since interfacial tension in W/W interfaces is often extremely low and adsorption of small molecules is very weak. Consequently, W/W emulsions are prone to coalescence, which cannot be slowed down by conventional surfactants. However, W/W can be properly stabilized by particles adsorbed on the interface, and many examples of Pickering W/W emulsions have already been reported.

These fat-free dispersions can be highly interesting for formulation of functional food products and oral delivery of active components [2]. The presentation will provide a review of our research works on this field. We used gelatin-in-maltodextrin W/W emulsions for the encapsulation of lactase (b-galactosidase) enzyme inside gelatin microgels cross-linked with genipin [3]. The enzyme showed a high degree of activity and gelatin microgels provided some protection against a simulated gastric fluid. Suspensions of such gelatin-genipin microgel particles, loaded with lactase, were preserved by freeze-drying and the original particle size was preserved after one cycle of freeze-drying and rehydration, maintaining an acceptable enzyme activity. However, the lactase enzyme lost its activity in acidic pH. More recently, we have designed gastro-resistant capsules by ionic complexation of BSA-in-alginate dispersions inside calcium alginate shells covered with a thin layer of chitosan [4]. These capsules were perfectly stable in a simulated gastric fluid but they dissolved very rapidly and released the BSA content in a simulated intestinal fluid. In another work, we have obtained multiple W/W/W emulsions in aqueous mixtures of water, gelatin and maltodextrin [5]. We prepared these W/W/W emulsions by a simple method that consisted in cooling down gelatin-in-maltodextrin (G/M) emulsions, leading to the spontaneous formation of inner maltodextrin droplets and producing M/G/M multiple droplets. The colloidal stability of M/G/M emulsions was much increased by the addition of mucin particles that adsorbed at the G/M interface. This was the first report of a simple one-pot method for the preparation of multiple W/W/W emulsions.

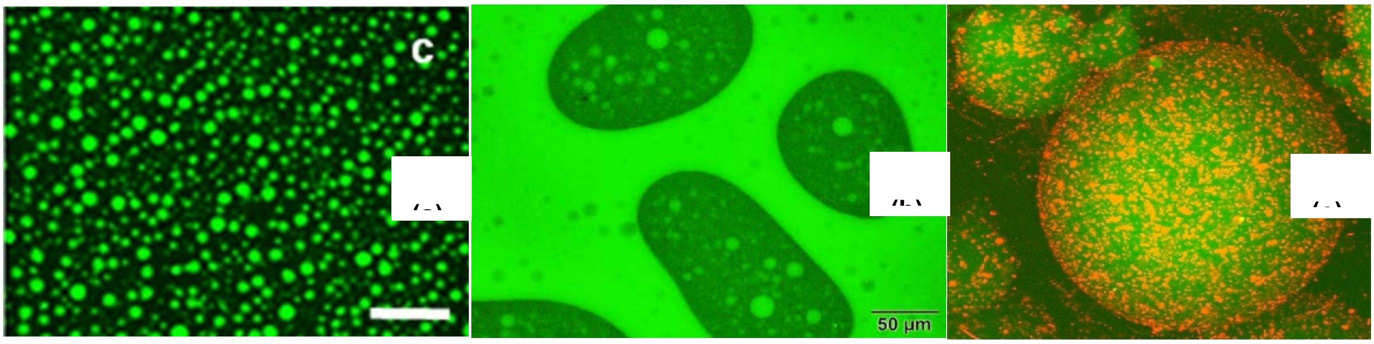

Fig 1. Examples of a water-in-water emulsion (a), a multiple water-in-water-in-water emulsion (b) and a water-in-water emulsion (c) stabilized with particles adsorbed at the interface**.**

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Gradient poly(2-oxazoline)s as a new class of biocompatible emulsifiers: Structure-property relationships and cosmetic application

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Over the past few decades, polyoxazolines (PAOx) have gained renewed interest as a potential alternative to traditional polyethylene glycol ethers (PEGs) due to their high biocompatibility, low toxicity, and greater tunability. However, their unique control of composition, chain length, and monomer distribution for use as emulsion stabilizers has not been extensively studied. The aim of this study was to evaluate the ability of both block and gradient PAOx to stabilize oil-in-water (O/W) emulsions while characterizing the resulting emulsions using granulometry, stability, and rheology studies to understand the structure-property relationship.

Surprisingly, stable O/W emulsions and high internal phase emulsions were obtained with just 0.5 wt% of PAOx. The most hydrophilic PAOx was found to stabilize the finest emulsions, allowing for an adjustment of their texture and consistency, as well as the concentration increase and oil content. The degree of polymerization played an important role in enhancing stability with a DP100 being optimal for maximum steric repulsion and adsorption at the O/W interface. Notably, emulsions stabilized by gradient copolymers performed similarly to systems stabilized by their block counterparts, providing an easily accessible one-pot statistical copolymerization process for the development of high-performance and biocompatible emulsifiers.

Finally, the high performance of gradient PAOx as polymeric emulsifier was illustrated by formulating a BB cream. PAOx has proven to be a better alternative to the polyethoxylated surfactant mixture typically used in such formulations.

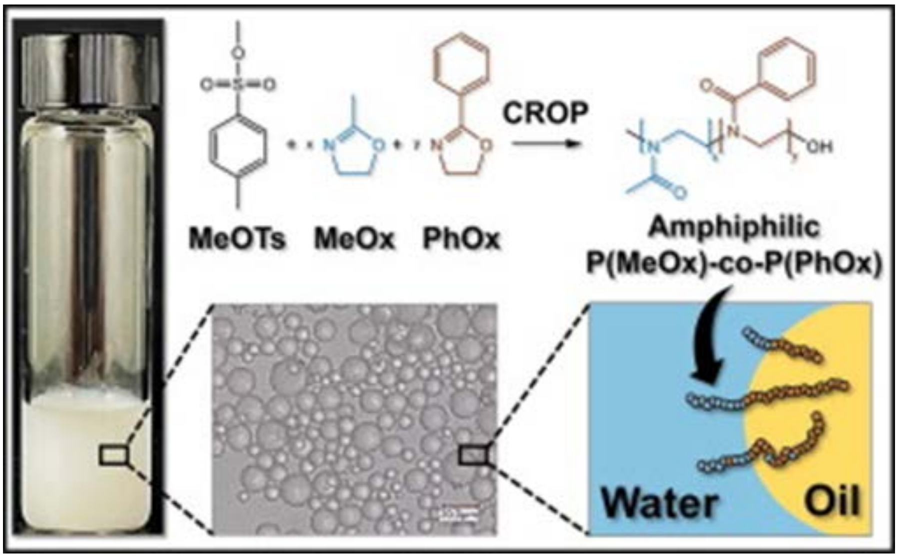

Fig 1. Synthesis of well-defined amphiphilic P(MeOx)-co-P(PhOx) and use as polymeric emulsifiers.

Methodology and preliminary steps to develop an innovative bioinspired cosmetic active ingredient

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In the context of a post-pandemic era, consumers are looking for naturalness and simple formulas. Natural ingredients are being associated with the ideas of safety, efficacy, well-being and as being more respectful of health and the environment[1]. To meet the evolving needs of consumers, the development of innovative natural ingredients is at the heart of the cosmetics sector's concerns.

This development must be anchored in the principles of sustainable development and must also respect the regulatory framework to preserve the natural resources of the planet and the agreement between countries for the protection of natural raw materials. They also must be scientifically innovative, whether that be with a greener process, a pioneering raw material or an innovative biological property. In order to be more innovative, bioinspiration is being introduced into the field of natural ingredients. In fact, since organisms have existed on Earth for about 3.8 billion years, they have shown that they are capable of adaptability to solve problems such as drought and UV radiation. In the quest for innovation, it is becoming increasingly important to draw inspiration from Nature to imagine innovative solutions to new challenges.

The purpose of this research is to set up a methodology that helps cosmetic companies to develop natural and innovative cosmetic active ingredients. More specifically, this research targets active ingredients bioinspired by plants. This methodology suggests different approaches to finding bioinspiration in plants. It then outlines the steps for the development of the active ingredient. Starting from considering the different regulations and protection laws that exist in the world and which frame this type of development, this research also draws the path of the following steps of development once the plant of interest is selected[2]. Steps such as the classic extraction methods of the active ingredient, characterization of the phytochemical profile with a combination of analytical methods (HPLC-DAD/DED/HRMS, GC-MS/FID, NMR,…), evaluation of the efficacy of the extract with biological activity assays, optimization of extraction process and the transition to greener eco-extraction conditions are discussed. Finally, this methodology describes the main methods used for the formulation of a plant-derived natural ingredients: discoloration, deodorization, remove of contaminants and addition of a cosmetic support. Overall, the methodology presented in this research facilitates the development of an innovative bioinspired natural cosmetic active ingredient.

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Theoretical and experimental approaches of extraction. Developing multiple solvents systems and deep eutectic solvents for the optimisation of extraction and solubilization of volatile or nonvolatile compounds

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Sustainability-driven search for alternative solvents has led to the development of more complex liquid phases, such as ionic liquids and deep eutectic solvents. In both cases, because such solvents are composed by at least two distinct and unrelated species, namely 1 cation and 1 anion in the case of an ionic liquid, and 1 acceptor and 1 donor of hydrogen bonds in the case of a deep eutectic solvent (DES). This leads to a very significant increase in potential solvents available, and makes it more tedious to find experimentally a solvent best-suited for a given application.
Adding the fact that in the field of natural compounds extraction and purification, there is also a great diversity in molecules of interest to extract, whether volatile or non-volatile, renders the task of optimizing a solvent for a given target molecule even harder and more time consuming.

In such a case, the development of a modelling tool, such as COSMOTherm, has become very benefitable for researchers and crucial for increasing research kinetics.

In this talk, we will present various studies centred around the development of sustainable solvents for the extraction/purification of natural compounds. Study of the formation of new eutectic solvents will be evoked, as well as several applications of eutectic solvents-based systems for the extraction of polyphenolic compounds from kiwi peels, the absorption of volatile compounds using natural type-V deep DES and of the development of biphasic multiple solvents systems for the development of a purification technology called centrifugal partition chromatography.

Theoretical and experimental results will be presented hand in hand and the adequacy between these two approaches will be discussed.

Elaboration and characterization of capsules from the polymerization of Pickering emulsions stabilized by cellulose nanocrystals

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Cellulose nanocrystals (CNC) are biorenewable particles of rising interest for the stabilization of Pickering emulsions. They are commonly extracted from cellulose substrates, and are needle-shaped nanoparticles (150-200 nm in length, 5-20 nm in width)[1]. In the present work, direct[2], inverted[3] and double[4] Pickering emulsions were stabilized using surface modified CNC. Taking advantage of this modification, the stabilized emulsions were further polymerized by whether free or controlled radical polymerizations leading to objects with a very broad range of morphologies depending on the polymerized phase and initiation locus. Suspension polymerization of water-in-oil emulsions lead to either full beads (matrix capsule) or empty capsules (core capsules). Likewise, elaboration of a new type of capsules (hollow/porous microcapsules) was investigated, by using double emulsions as template and polymerizing their intermediate phase. The benefits of this strategy are that the polymerization only occurs in the intermediate phase and therefore does not interfere with the encapsulated compounds.
The presentation will focus on the elaboration of those capsules and their characterization in terms of morphology, mechanical resistance and encapsulation ability.

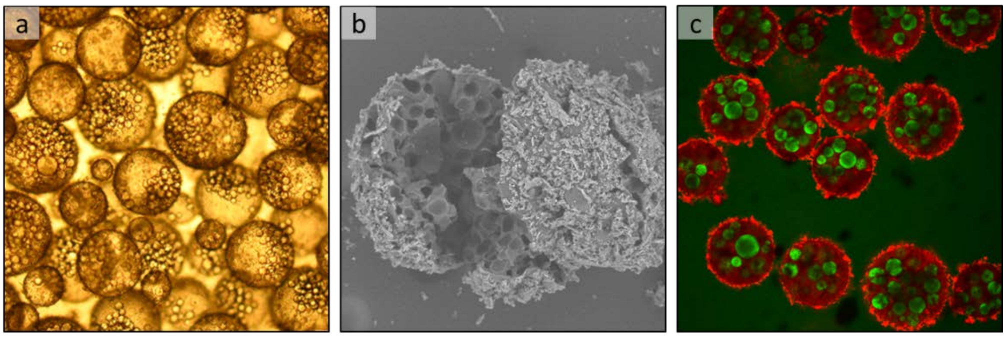

Fig 1. CNC-stabilized Pickering double emulsions, a) before and b) after polymerization, c) encapsulating both hydrophilic and lipophilic dyes.

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Pickering emulsions stabilized by Oppositely Charged Particles

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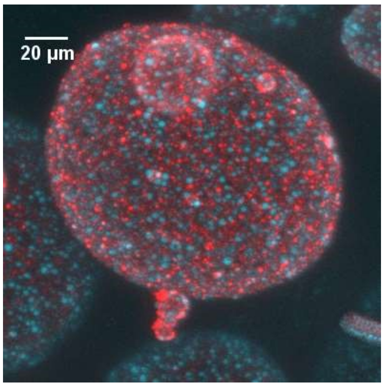
For ecological concerns, many industries are facing the challenge of simplifying their formulations. In this context, emulsions stabilized by colloids rather than surfactants, known as Pickering emulsions, are a promising trail. But the simultaneous use of different particles as emulsifiers was rarely investigated. In the present work, Pickering emulsions made with Oppositely Charged Particles (OCPs) were studied.

Anionic and cationic PMMA-based copolymers particles have been designed and used separately or in mixture to stabilize o/w Pickering emulsions (Fig.1A). The influence of the stirring rate on emulsion characteristics (droplet size and morphology, rheology, stability) was also investigated.

The droplet surface coverage by the particles was deduced from the droplets' diameter. It was demonstrated that the adsorption rates of the particles at the droplet surface, during the emulsification, influenced both the coverage and the morphology of the droplets. Hence, different rheological properties and stability profiles of the emulsions have been observed (Fig. 1B). The use of OCPs combined with an appropriate stirring speed allowed controlling the emulsion characteristics. At low stirring rate, a faster particles adsorption occurred due to the formation of aggregates. This resulted in emulsions with small and poorly-covered spherical droplets, especially at the charge stoichiometry of the particles. Oppositely, at high stirring rate, non-spherical and moderately-covered droplets were obtained. Finally, thermal ageing tests demonstrated that OCPs emulsions were particularly stable over time.

This work highlighted the interest of designing Pickering emulsions with a binary mixture of OCPs. Topical drug delivery could be a direct application of such systems as the droplet coverage by the particles can regulate the release rate of encapsulated substances [1] and their delivery into a specific layer of the skin [2].



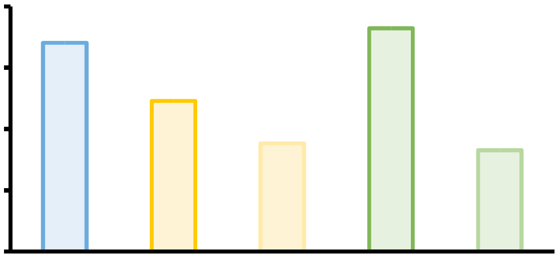


Fig 1. (A) Confocal microscopy image of oil droplets stabilized by cationic particles (in red) and anionic particles (in blue) (B) Storage modulus G' measured at 1 rad/s for Pickering emulsions obtained with different droplet coverages (S stands for spherical and NS for non-spherical droplets).

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The mechanism of bilayer permeation of oil-soluble substances with bile salt

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Oil-soluble substances ingested orally are absorbed after they are solubilized into mixed micelles composed mainly of bile salts in the small intestine. We have previously used giant unilamellar vesicles (GUVs) composed of phospholipids as a cell-size model and investigated the morphological changes induced by the addition of bile salts in terms of confocal laser scanning microscopy (CLSM)1). In this study, we prepared GUVs with a mixture of phospholipids and cholesterol to better mimic plasma membranes and examined the effect of cholesterol on the morphological changes in GUVs induced by bile salt micelles. Furthrermore, we studied a bile salt-mediated absorption of oil-soluble nutritional substances by using CLSM.

GUVs were prepared by gentle swelling method of dry solid films with mixtures of 1,2-Dioleoyl-*sn*-glycero-3phosphocholine (DOPC) and Cholesterol (Chol), in which the Chol contents were 0, 12, 19, 33 mol%. Sodium cholate (SC) was used as a representative bile salt. Texas-Red was doped in mixed lipid to observe bilayer membrane. Morphological changes in GUVs by the addition of SC (concentrations: 0.5, 1.5, 3.0, 5.0, 7.5,15, 20 and 25 mM) were observed by CLSM. The interaction between GUV and SC was evaluated by isothermal titration calorimetry (ITC) measurements. Monoolein (MO) and oleic acid (OA) were used as oil-soluble nutritional substances.

1) The effect of bile salt addition on morphology of phospholipid/cholesterol liposome

The morphological changes of phospholipid/cholesterol liposome by addition of sodium cholate (SC) solution prepared at 8 levels of concentration were observed using CLSM. As the concentration of SC solution increase, there are four patterns of morphological changes ; pattern (a) "formation of small vesicles inside GUVs", pattern (b) "formation of thread-like lipids outside GUVs", pattern (c) "decrease in particle size while maintaining the shape", and pattern (d) "disappearance of GUVs by solubilization". This change was similar to the result in the DOPC alone GUV, but the SC concentration at which solubilization occured shifted to the higher concentration side with the addition of Chol. In other words, the solubilization of GUV was suppressed by Chol.

2) Interaction of SC monomer and micelle with phospholipid/cholesterol liposomes evaluated by ITC measurements

In the case of low SC concentrations at which SC exists as monomer, endothermic changes were observed due to hydrophobic interactions associated with the distribution of SC molecules into the bilayer. On the other hand, at higher concentrations at which SC exists as micelles, exothermic changes were observed, indicating interactions between SC micelles and polar groups of the bilayer2). Furthermore, the addition of Chol to bilayer shifted the peak of the exothermic reaction toward the higher SC concentration. These results indicate that the morphological changes of GUV depend on the dissolution state of SC and that the addition of Chol suppresses the solubilization of GUV by SC micelles.

3) The mechanism of bilayer permeation of oil-soluble nutritional substances with bile salt

The results showed that the oil-soluble substances are absorbed to the inside of GUV as smaller vesicles according to the process of pattern (a). Furthermore, it was found that when Chol was mixed with DOPC, the time required for incorporation of the oil-soluble substances into the GUV increased.

In conclusion, the dissolved state of bile salts and the amount of Chol added to GUV are shown to affect the membrane permeation of oil-soluble substances.

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Diclofenac recovery from aqueous solutions by emulsion liquid membranes

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Diclofenac (DCF) is a non-steroidal anti-inflammatory drug that generates ecotoxicological effects in living species when is released in aquatic environment. Aquatic animals, plants, birds, amphibians and mammals may suffer a significant deterioration in the organ function, acute cell poisoning and even death[1]. Therefore, it is necessary the application of effective methods for DCF removal of polluted water. Emulsion liquid membranes (ELM) technique is an interesting alternative for this purpose because allows the extraction and simultaneous recovery of a target molecule through a W/O/W double emulsion. The extraction occurs when the molecule is transferred from an outer aqueous phase (OAP) to an organic phase OP (composed by carrier, surfactant and solvent) and, subsequently, it arrives to an inner aqueous phase (IAP), composed by a stripping agent, for its recovery. The mass transfer is carried out at high speed through a membrane phase with high surface area, making use of a small volume of organic phase[2]. Figure 1 shows a scheme with the ELM configuration and a DCF mass transfer representation in the system. Accordingly, a ELM system was established using n-trioctilamine (TOA) as carrier, Abil ® EM 90 as surfactant and n-dodecane as solvent in OP, as well as NaOH for the stripping phase (or IAP). A W/O emulsion was formed with these phases, shaking at 15000 rpm during 10 min and later it was poured into OAP with DCF (50 mg/L), at pH 5. The double emulsion is formed shaking at 300 rpm during variable time, allowing mass transfer to occur. It was studied the effect of various parameters in the system, such as surfactant (0.5-7% w/V), carrier (0-5% w/V) and NaOH (0.01-0.20 mol/L) concentration, extraction time (5-80 min), emulsification time (3-10 min) and speed (10000-17000 rpm). It was observed that a low concentration of surfactant generates an unstable membrane and a larger quantity cause a smaller droplet size, which is related to a greater surface area available for mass transfer. A membrane composed of TOA 5% w/V and Abil ® EM 90 2% w/V dissolved in dodecane was able to completely remove DCF from OAP in 15 min by a double mass transport mechanism: reactive and physical extraction, by interaction with TOA and dodecane, respectively[3]. The same system obtained 18.45% of recovery with NaOH 0.10 mol/L after 30 min. The stripping step was considerably slower than the extraction step, which was attributed to the surfactant presence into membrane phase and its interaction with TOA that favors the interface rigidity, hindering the arrival of solutes to the internal aqueous phase. Hence, the maximum recovery obtained was 30.06% in absence of TOA and less than 80% of extraction. In addition, it was proved that emulsification speeds and times lower than 15000 rpm and 10 min, respectively, generate larger drop diameters and smaller superficial area. The results showed that this technique can be applied to remove DCF from aqueous media in a few minutes with a simple system, which would considerably reduce the environmental impact produced by the presence of this drug in aqueous effluents.

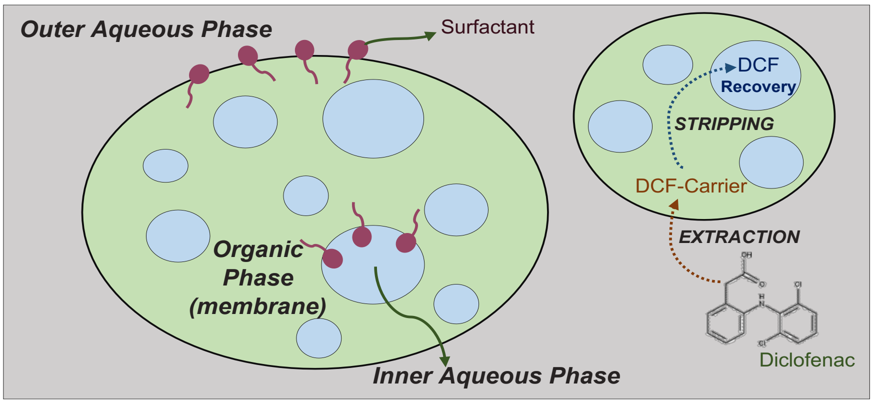

Fig 1. Conformation of ELM and DCF mass transfer in the double emulsion system.

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Morphology controlled nanomaterials to navigate mucosal barriers

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Drug delivery to mucosal barriers is preferred in comparison with invasive parenteral routes. However, designing drug carriers to avoid dilution with physiological fluids and mucus clearance still represents an unmet challenge. Nanomaterials (NMs) coated with mucoadhesive polymers have shown their ability to partially address these problems due to their small size and mucoadhesive surface. However, while NM size and surface properties have been extensively studied, there is a lack of investigations on the morphology-dependent behaviors of NMs toward mucosal barriers. The strategy we envisioned is to consider the morphology of NMs as a relevant parameter to reach mucus avoiding dilution with biological fluids, accumulating at high concentrations close to the mucosal epithelium and internalized by epithelial cells. Understanding whether NM morphology impacts their transport into the mucus and mucoadhesive behaviors requires robust technological tools to manufacture NMs with controlled properties. In this context, our research group has recently developed complementary processes to design morphology-controlled NMs with simultaneous control of aspect ratio, size, and versatile surface modification. Nonspherical particles, denoted as nanoplatelets, were formed by supramolecular and hierarchical self-assembly in water of polysaccharides hydrophobically modified with palmitic acid and α-cyclodextrin. Nanoplatelets have flat surfaces, sharp edges, and a high aspect ratio (~20), as characterized by AFM. We revealed that NMs with a nonspherical morphology exhibited different physical and biological behaviors than spherical particles. Indeed, the nanoplatelets had faster mobility in biological fluids and higher cell internalization. They exhibited faster bioadhesion than spherical particles. Using real-time in vivo imaging on a rat model, we revealed that nanoplatelets had a longer residence time in the intestine and in the bladder compared to spherical particles. Finally, we showed that the nanoplatelets did not exhibit the same biological behaviors as spherical particles to treat mucosal infections and inflammation.

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Exploring ageing, network stresses and gravitational stability in model suspension formulation systems

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Stability of formulated products is complex to predict, especially regarding gravitational stability of suspensions. It is an important challenge for a wide range of industries including dispersion products for coatings, foods and crop protection.[1] A key challenge here is visualising the microstructure within the formulated products that governs their gravitational stability and how it ages with time. We address this by designing a model refractive index matched PDMS emulsion in aqueous-glycol media with non-adsorbing polymers that represents the key features of commercial suspension products and investigate its ageing at the microscopic scale using confocal microscopy.

Confocal microscopy provides a real space observation of dynamics down to a single particle level. The nonadsorbing polymer causes weak aggregation of the PDMS droplets into a space filling network that provides mechanical stability against gravitational separation.[2] By mixing a dense oil component -- pentafluorotoluene with PDMS, we are able to tune the density difference, and thus the collapsing time for capturing the process. Phenomenal observation including gel arm coarsening, fluid channel development, and interface formation, is done in a relatively large scale (2 cm-height cell more representative of normal sized samples). At higher resolution, combined with a solvatochromic dye in the oil phase, particle contact information is linked to interparticle forces within the gel network.[3-4] The distribution of high contact volumes indicates the areas where the stress is concentrated. During the ageing process, we investigate the role of stress, explore its correlation with dynamics, and investigate gravitational instabilities.

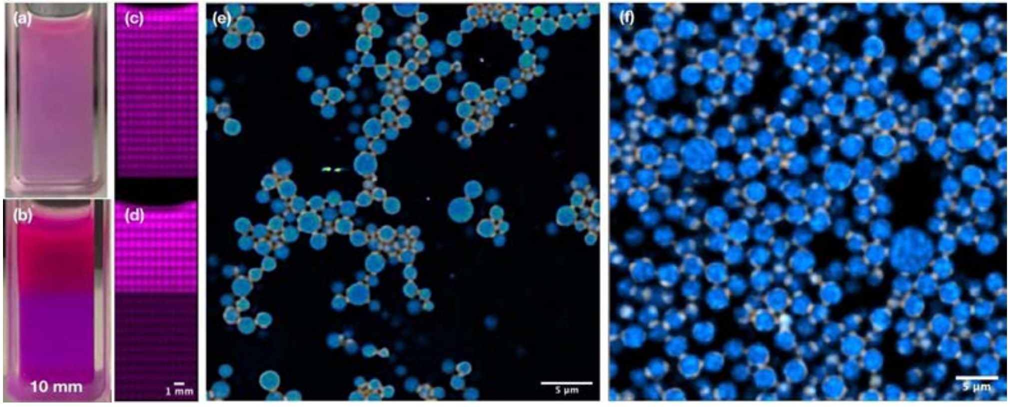

Fig 1. (a-b) a 2 cm-height gel sample before and after collapse, (c-d) under confocal microscope, (e) at higher resolution, particles and their contacts, providing stress information within the gel system, (f) a collapsing gel losing its original structure.

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Formulation optimisation assisted by AI-based optimisation algorithms

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Formulation optimization is often a time-consuming task, often performed by trial-and-error methodology, modifying one variable at a time, which is very inefficient.
Recently, Bayesian optimization has been shown to outperform human decision-making for the optimization of chemical reactions and formulations. It is well-suited for formulation optimisation problems, for which the evaluation (experiment) is expensive and long.
In this project we address the problem of formulation optimization with continuous and categorical variables.
We propose a Bayesian optimization method that uses a covariance function specifically designed for categorical and continuous variables and initially proposed by Ru et al. in the COCABO method.
We also experimentally compare different methods of optimization of the acquisition function. We measure their performances in the optimization of multiple formulation simulators.
We find that a brute-force approach for the optimization of the acquisition function offers the best results but is too slow when there are many categorical variables or categories. However we show that an ant colony optimization technique for the optimization of the acquisition function is a well-suited alternative when the brute-force approach cannot be (reasonably) used.
We show that the proposed Bayesian optimization algorithm finds optimal reaction parameters in fewer experiments than state of the art algorithms on our simulators.

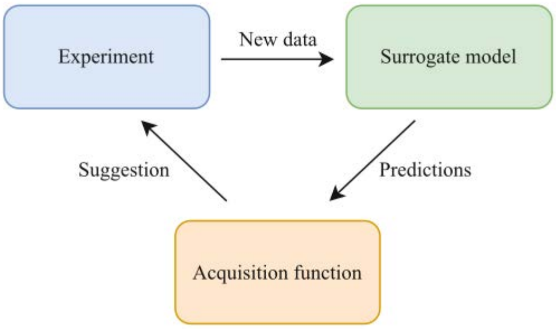

Fig 1. Caption

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A novel hybrid artificial intelligence approach for optimizing the formulation of calcined clay cements

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Cements based on calcined clay have several environmental advantages over traditional cements. Firstly, they require less energy for production as they can be manufactured at lower temperatures than traditional cements, resulting in a reduction in greenhouse gas emissions associated with cement production. However, formulating these cements can be complex due to the variability of specifications and formulation parameters. Trial-and-error and experimental designs can be costly and time-consuming due to the high number of variables involved. Therefore, using artificial intelligence (AI) can be useful in optimizing the composition of materials.

Predictive modeling techniques based on AI can be used to simulate material properties before production, enabling scientists to quickly test various formulations virtually. The objective of this study is to use a novel hybrid AI approach to optimize the formulation of calcined clay cements. An AI model incorporating physically-informed artificial neural network and chemical reactivity ratios was used to predict cement properties (Fig. 1). The model's hyperparameters were optimized using a Bayesian approach. The results of AI application allowed for the identification of an optimal formulation zone in the ternary system of calcined clay, limestone, and clinker. And the alumina to silica chemical ratio of the clay being the most impactful parameter on compressive strength.

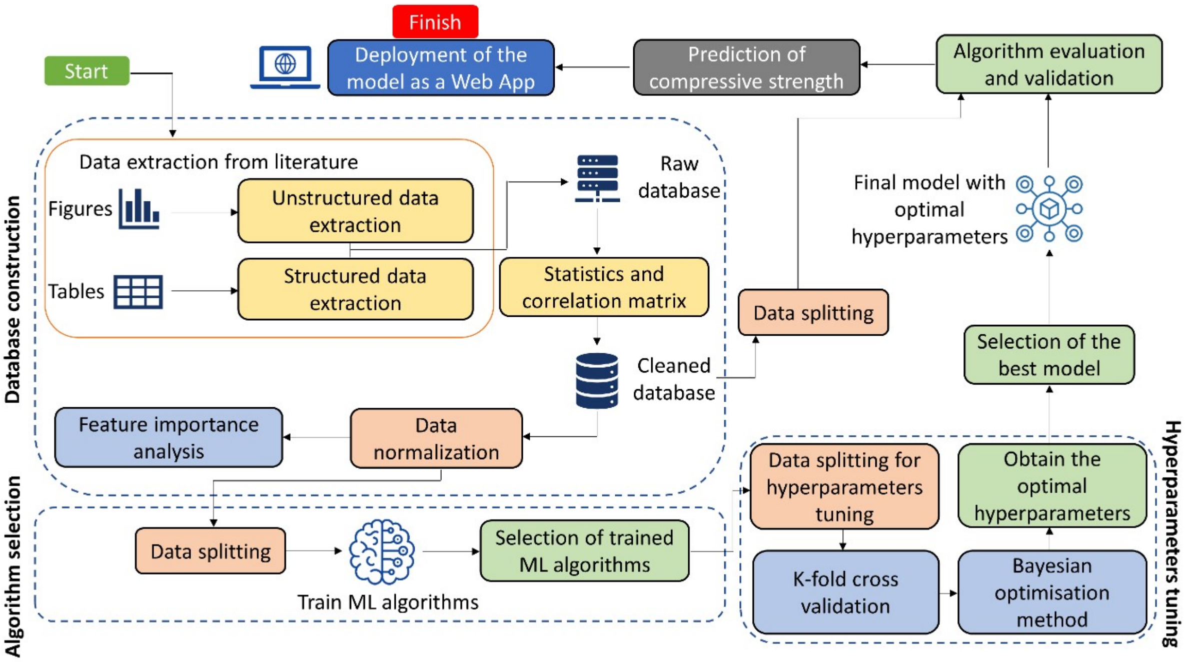

Fig 1. Steps for the application of artificial intelligence models in the formulation of calcined clay cements.

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Immobilization of organic nuclear waste in Pickering emulsions: formulation and characterization

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The immobilization of organic nuclear waste is a critical challenge facing the nuclear industry, due to the complexity and variability of the waste streams, the potential for chemical reactions and degradation, and the need to ensure long-term stability and safety. The primary goal of nuclear waste immobilization is to isolate the waste from the environment, and is typically achieved by incorporating the waste into a solid matrix. Geopolymers, which are inorganic aluminosilicate cements, has recently been applied efficiently to nuclear waste, where the organic liquid is permanently confined under the form of micrometric droplets [1]. As the immobilization conditions into geopolymers are highly alkaline, unwanted hydrolysis reactions of organic compounds (vegetable oil or tributyl phosphate) may occur [2]. resulting in leaching of the organic compounds. Therefore, pre-treatment methods for these hydrolysable wastes must be carried out bore the incorporation into matrices. To avoid hydrolysis reactions, one way is first to build a protective shell around the drops of organic liquid and then to introduce these encapsulated drops in metakaolin suspension. To build this protective shell, we used aluminosilicate nanoparticles (zeolites) as Pickering [3] particles. This had the triple advantage of stabilizing the emulsion, protecting the organic compound and ensuring compatibility with the geopolymer.
In this study, we explore the use of Pickering emulsions stabilized by nanoparticles, such as zeolites LTA nano, as a potential solution for the immobilization of organic nuclear waste. After particle synthesis, Pickering emulsions are prepared using a model organic liquid waste simulant (sunflower oil and tributyl phosphate) and zeolites LTA nano (Figure 1). The emulsions were characterized using a range of techniques, including optical microscopy, dynamic light scattering, and zeta potential analyses. We also investigated the effect of various formulation parameters, such as the particle size and concentration of particles on the emulsion stability and waste loading capacity. A geopolymer was then formulated in order to study the leaching of organic compounds and the durability of materials.

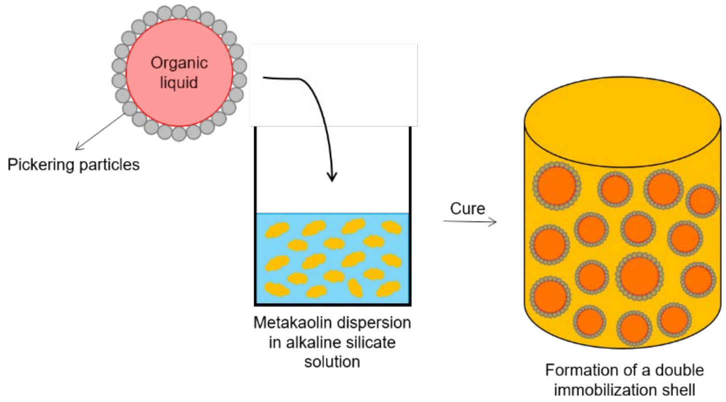

Figure 1. Illustration of the formulation of Pickering emulsions before immobilization in geopolymer matrix

Our results indicate that Pickering emulsions could be a promising approach for the immobilization of organic nuclear waste, with a high waste loading capacity. The emulsions were found to be stable for up to 30 days, with no significant changes in their particle size or zeta potential over time. We also found that the emulsion stability and waste loading ability were affected by the concentration and size of the nanoparticles used.

However, further studies are needed in order to evaluate the long-term stability and safety of these emulsions for nuclear waste management applications.

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Sustainable Liquid-liquid extraction of metals using hydrotropes as extractants

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Nearly all discussions about distribution coefficients of salts between an “aqueous” and a “solvent phase in liquid-liquid extraction refer to hypothetic supramolecular complexation constants and derive apparent stoichiometries from dilution experiments. Complexing molecules are (nearly) water-insoluble, surface-active agents with a charged or solvated polar head-group that has an affinity to cations.
In the present study, we investigated for the first time the replacement of a toxic and scarcely biodegradable extractant by sodium salicylate, a solid hydrotrope (1). Even if metal-extractant complexation is weaker than with a classical extractant, the extraction is still efficient. Moreover, the distribution coefficient can be adjusted without varying the acidity, in contrast to nearly all current hydrometallurgic processes. Here, the complexation is no more dominant, but complemented by other molecular forces, including organization of the ternary solution in the water-rich and solvent-rich corner of the phase diagram (2). In the example chosen, we will describe the structures occurring around the ten tie-lines and explain why only three of them are located in the region favorable to the design of a liquid-liquid extraction process, illustrated by the region labelled in green on the left side of the figure.
The explanation is given by the “ienaic” decomposition of the Gibbs energy of transfer. This multi-sscale approach includes entropy and generalizes the mass action law in a more general multi-scale quantitative approach that has some predictive power (3). Using this ienaic approach instead of modelling with multiple competing first neighbor equilibria will allow design of efficient liquid-liquid extraction using synergy as well as non-classical, but self-assembling molecular systems.

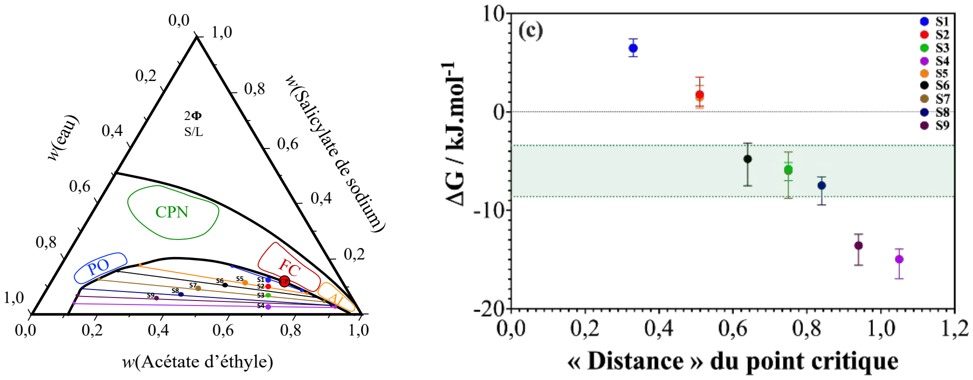

Fig 1 : Liquid-liquid extraction used in ten different formulations in an oil-water miscibility gap. (Left) position of the tie-lines in the ternary phase triangle at room temperature compared to the different local nanostructures evidenced in organized ternary fluids: PO means pre-ouzo aggregation present; FC means hetero-phase critical fluctuations dominant, CPN means prenucleation clusters present and AI means inverse aggregates; (right): The Gibbs energy of transfer of a rare earth nitrate is far from the values expected considering the supramolecular complexation in the solvent only and is linear over several decades with the thermodynamic distance of the considered tie-line to the critical point.

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Characterization of aqueous two-phase systems for arsenic removal

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Nowadays one of the first contaminants is arsenic according to the Environmental Protection Agency. Therefore, there is an urgent need to develop efficient methodologies that follow the principles of green chemistry for its removal. For this reason, this project works with aqueous two-phase systems (ATPS), extraction systems that present great potential for a variety of analytes, they are simple, have low-cost operation, and are environmentally friendly systems. In recent years, a significant number of papers have been published in which ATPS have been applied for the extraction of biomolecules and metal ions. The recovery of acids (as is the case of H_3AsO_4), has been little addressed using ATPS. Many publications report the conditions to achieve a high extraction of the species of interest without deeply analyzing the interactions that allow mass transfer. Therefore, it is essential to elucidate the way in which the interactions between the species to be extracted and the components of the ATPS occur.

In this work, polymer/salt systems composed of PEG 1000, sodium salts (Na_2SO_4, Na_2HPO_4 and $Na_3C_6H_5O_7$) and H_3AsO_4 as the molecule to be extracted were used (1,2). Binodal curves were generated for all the systems with the three different salts, in the absence and presence of H_3AsO_4, the analysis of these curves allowed to find the optimal conditions to generate the phase breaking in the aqueous systems and based on the results obtained, be able to select the ATPS for the extraction of arsenic. It was decided to work with ATPS composed of 5% (w/w) PEG 1000, and 28% (w/w) of Na_2HPO_4, 22% (w/w) in the case of Na_2SO_4 and 30% (w/w) using $Na_3C_6H_5O_7$. All these concentrations were the optimal ones to achieve phase breaking and were obtained from the binodal curves. With PEG 1000 the best results were obtained. Varying the initial concentration of H_3AsO_4, an extraction percentage of 56% is achieved, which is obtained when Na_2SO_4 is used; while with Na_2HPO_4 it is possible to extract up to 42% of arsenic and with sodium citrate up to 15%. It is important to highlight that there are significant variations in the pH values of each system using the three sodium salts, indicating not only the presence of the neutral arsenic species, but also of the anionic species. With sodium sulfate there is a pH of 2.3, with sodium citrate a pH of 6 and 7.5 with sodium hydrogen phosphate. These variations in pH are responsible for the behavior in the extraction of arsenic. It is proposed that the transfer of the neutral species H_3AsO_4 to the polymeric phase occurs through a PEG solvation mechanism using sodium sulfate. The Raman spectroscopy characterization was also made for each ATPS describing in detail every signal in the spectrum and showing that effectively using sodium sulfate there is a band at 766 cm^{-1} that corresponds to the neutral species H_3AsO_4, (3,4) which indicates that the species is transferred from the saline phase to the polymeric phase as a neutral species H_3AsO_4 interacting with PEG through a mechanism of solvation.

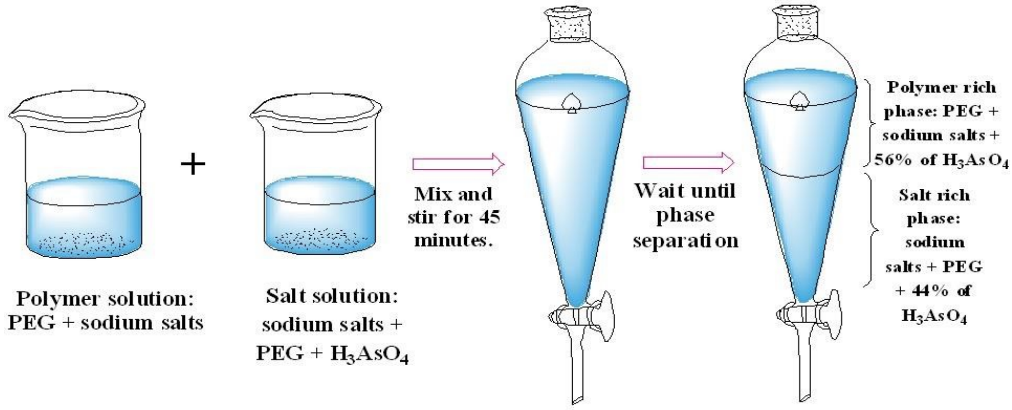

Fig 1. Aqueous two-phase system for arsenic removal.

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Energy storage systems: Optimize formulation and fabrication

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Energy storage systems are everywhere in our everyday life and optimizing their performance is a key point to control. The performance of a battery is heavily dependent on its formulation and its fabrication process. It can affect its energy density, power density, cycle life, safety, and cost.

Optimizing battery features and fabrication is important for several reasons:

- Improved performance: Improving the battery features and fabrication can lead to improvements in the battery's energy density, power output, and cycling stability. This can make the battery more efficient, reliable, and cost-effective.
- Reduced cost: Optimizing the battery fabrication process can help reduce manufacturing costs by improving production efficiency and reducing waste. This can make batteries more affordable for consumers and accelerate the adoption of energy storage technologies.
- Increased safety: Enhancing the battery design and fabrication can improve safety by reducing the risk of thermal runaway, short circuits, and other safety hazards. This can help prevent battery fires and explosions, which can be dangerous and costly.
- Last and not least, environmental benefits by reducing the use of non-renewable resources and minimizing waste. This can help mitigate the environmental impact of battery production and disposal.

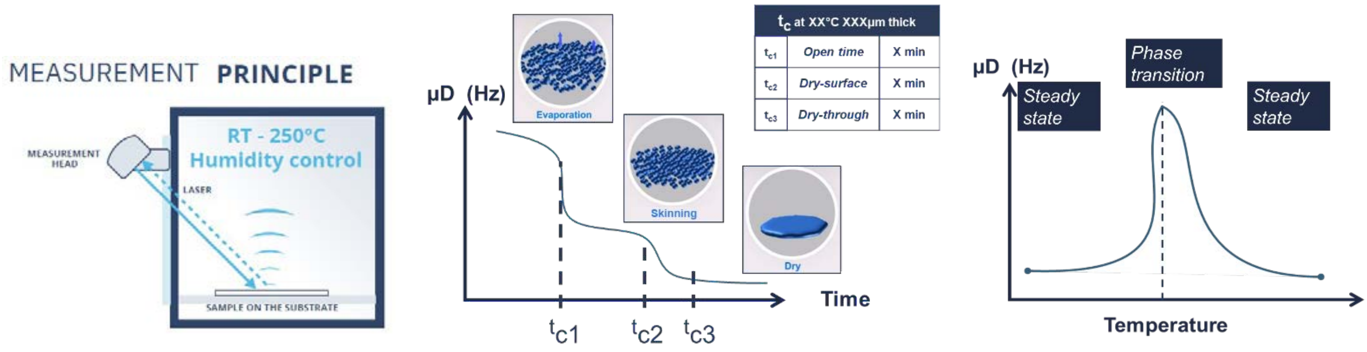

Fig 1: Measurement principle and results example

We will present a new in-situ, non-invasive, and handy method to compare different formulations and optimize the fabrication process.

Replacing a PFAS surfactant for a biodegradable blend in a highly oxidative triiodide solution used for gold etching in semiconductor manufacturing

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In the fabrication of microelectromechanical systems (MEMS), gold is an important material because of its great electrical and thermal conductivity properties, resistance to corrosion, solderability, and bondability.[1] It can easily be deposited by either dry (sputtering and evaporation) or wet (electroplating) methods.[2] Wet etching is an important process for patterning surfaces in device fabrication and the solution's wetting properties are paramount, especially when treating hydrophobic surfaces.[3] Iodine based chemistry is well known for gold etching[1] and Technic France offers this type of chemistry in its TechniEtch ACI2 formulation. In this product, a per- and polyfluroalkyl substance (PFAS) was used as a surfactant with its unique attributes (compatibility, stability, wetting properties) which makes them essential in the semiconductor industry.[3] However, PFAS are identified as a threat to human health[4] and the environment,[5] and there is a need to prospect for alternatives urgently.

In this study, we have successfully replaced the PFAS surfactant in the TechniEtch ACI2 formulation for a blend of biodegradable surfactants without compromising the performance of the solution in semiconductor manufacturing. To achieve this, a screening of surfactants and their compatibility in the mixture were tested and UV-visible spectroscopy was used as a method to quantify triiodide in solution. After thoroughly selecting a family of biodegradable surfactants, some of these were found to excessively foam, a hindrance in the manufacturing processing tools. Therefore, a mixture DOE analysis was performed to develop a blend reproducing the original PFAS surfactant properties with respect to five response variables: contact angle, dynamic wetting, and surface tension for wetting properties, and foam height and dissipation for foaming properties. Finally, this solution was studied at laboratory scale in a nano-structuring process to confirm its wetting properties and gold etching capabilities by scanning electron microscopy (SEM).

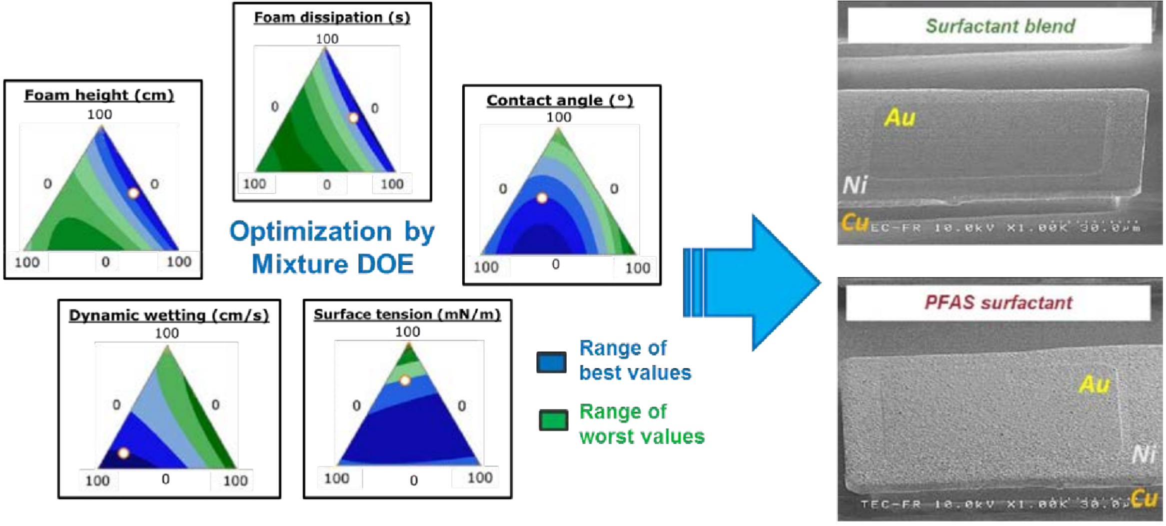

Fig 1. Ternary surfactant mixture DOE (target values in orange circles) and SEM images on gold nanostructure after etching. Best values in dark to light blue color-scaled to worst values in light to dark green.

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Influence of low water content on the thermo-physical properties of deep eutectic solvent choline chloride-urea and its application to colloidal dispersions

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Deep eutectic solvents (DES) are complex liquids that can be explored as possible alternatives to ionic liquids, with similar solvation or conductivity properties but with often bio-sources initial components. However, even more than for ILs, their physico-chemical characteristics can be partially missing or lead to scattered results in the literature.

The motivation of this work was the possibility to obtain and understand dispersions of nanoparticles in DES for thermoelectricity, as already studied in ILs [1]. To reach this goal, we focused on a classical DES, choline chloride-urea (ChU) [2] and measured viscosity and density, in a temperature range 20-45°C, in the presence of small amounts of added water. Indeed, for the development of practical use of such solvents out of glove boxes, the control or at least consideration of atmospheric humidity uptake is of tremendous importance. By extrapolation, we could then precisely describe the solvent in its driest state. From those measurements, a thermodynamic description for the viscous flow and the solvent structure at the molecular scale was proposed.

In a second step, 10 nm maghemite nanoparticles g-Fe_2O_3 were successfully dispersed in ChU. The stability of colloidal dispersions was examined in a multiscale approach, using visual observation, optical microscopy, dynamic light scattering and small angle X ray scattering. This successful stability showed that the description previously developed in ILs [3] could be extended to DES. In the absence of DLVO-type electrostatic repulsion, the structuration of the solvent at the solid/ liquid interface is indeed the key parameter to control in order to induce the long range repulsive force necessary to colloidal stability.

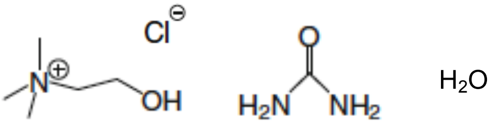

Fig 1. The 4 components of hydrated DES ChU : they have to form an adapted structure at the maghemite surface for colloidal stability

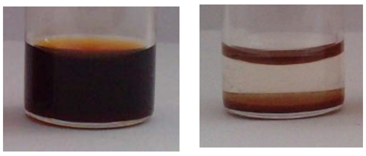

Fig 2. Stable/ unstable dispersions in ChU

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The application of sustainable surfactant-free microemulsions as reaction solvents

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Being the largest fraction in liquid-phase reactions, solvents contribute significantly to the overall toxicity potential of the process. Hence, there is a lot of research on applying water as a non-toxic, safe, sustainable, and cheap reaction solvent.[1,2] A common challenge poses the poor water solubility of substrates and catalysts. Inspired by nature, it is a common technique to use micelles to provide hydrophobic pockets in water and, thus, to overcome the solubility issues. The usage of surfactants, however, can lead to difficulties with regard to recycling, biodegradability, and foam formation.[1,3] For this reason, we study the applicability of sustainable surfactant-free microemulsions (SFMEs), consisting of water, a hydrotrope, and oil, as reaction solvents.

In this context, we successfully replaced a complex designer surfactant solution by a mesoscopic structured SFME as reaction solvent for transition metal- and enzyme-catalyzed reactions. Both reaction types are coupled in one pot, resulting in a chemo-biocatalysis tandem reaction. Moreover, the tandem reaction is performed in binary, unstructured aqueous solutions. Accordingly, no need for an interface can be identified, as previously assumed. Nevertheless, the SFME proves to be beneficial due to its excellent solubilization power.

In another approach, an SFME and a less structured binary mixture composed of food-grade compounds are applied as reaction solvents for the synthesis of nature-based vanillin. The rhizomes of the plant Curcuma longa serve as a natural source. Besides vanillin, vanillic acid and p-hydroxybenzaldehyde are synthesized that way, which are also found in the natural vanilla bean (see Fig. 1).[4] Both the extraction of the curcuminoids from the plant and the photochemical conversion to the flavors dispense with the usage of harmful chemicals.

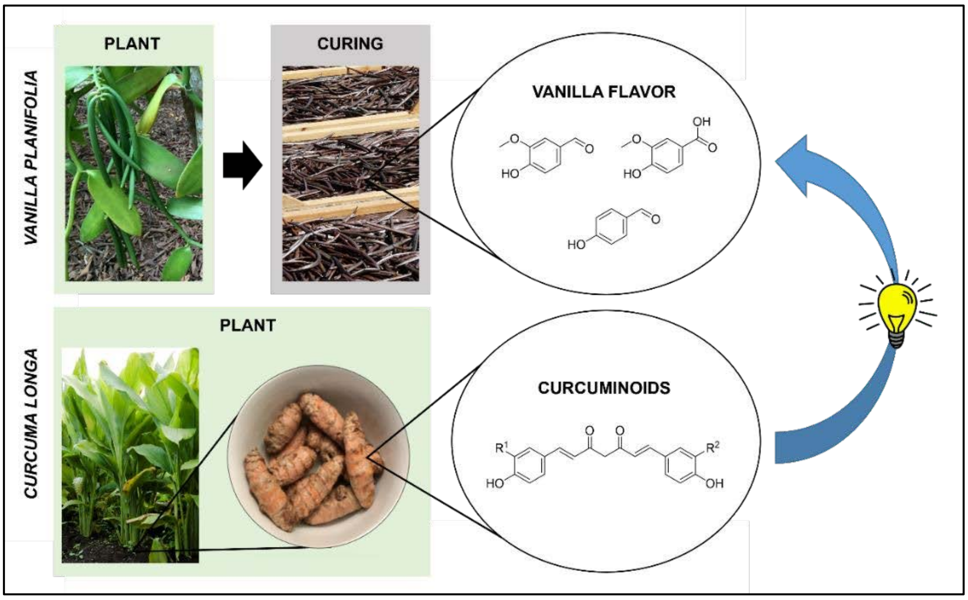

Fig 1. The photochemical production of natural-like vanilla extract from the plant *Curcuma longa* instead of *Vanilla planifolia*.

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Formulation of colloidal dispersions in ionic liquids for high temperature applications

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In colloidal dispersions in ionic liquid solvents (IL), the nanoparticles (NPs) combine their properties to this wide class of solvents with tunable properties, producing new types of complex liquids. ILs usually have low vapor pressures, and can have large electrochemical windows, high conductivity, and good thermal stability, depending on the nature of the cations and anions chosen. This latter property of several families of ILs opens new possible applications for colloidal dispersions in ILs at high temperature, from electrochemical devices to heat transfer fluids or thermoelectricity for example [1]. However, the formulation of such colloids in ILs, which are pure liquid salts, as well as their study is a challenge [2], especially at high temperature [3].
We show how stable dispersions of NPs, here nanometric iron oxides, can be obtained up to 200°C thanks to a proper choice of the interface between the NPs and the solvent. In this crucial interfacial region, the parameters to control and tune are the charge of the NPs, the nature and amount of the charged molecules added at the surface of the NPs as well as the preparation process. A system based on nanometric iron oxide nanoparticles in EMIM TFSI (ethyl- methylimidazolium bistriflimide) using several ligands combining a sulfonic or phosphonic group with an imidazolium group will be presented. Their nanostructure up to 200°C and after aging is analyzed by coupling chemical determination of the interfacial species (through phosphorus analysis), Dynamic Light Scattering (DLS), Small Angle X-Ray and Neutron Scattering (SAXS and SANS) and thermogravimetric analysis (TGA). The general guiding concepts to obtain such new complex systems with other combinations of solids and solvents will be summarized.

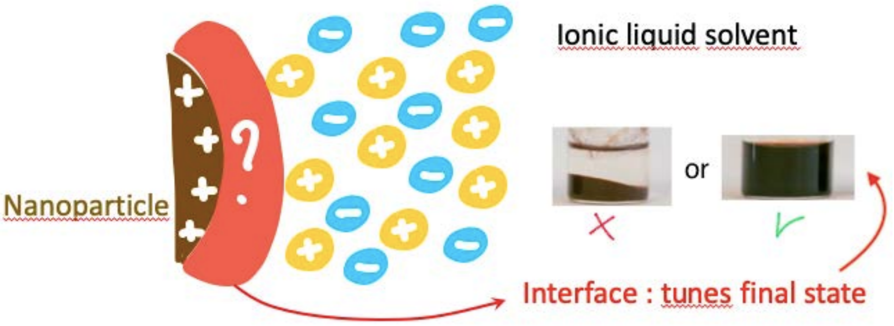

Fig 1. Challenge of the dispersion of nanoparticles in ionic liquids: the interface controls the final state, therefore the ability to keep particles in the solvent, even at high temperature.

5.

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Synthesis of gold nanoparticles in microemulsion and nano-emulsion systems using aqueous leaf extract of *C. chayamansa* as reducing agent

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In the present work, gold nanoparticles (AuNPs) were synthesized using microemulsion (μE) and nano-emulsion (nE) systems to control nanoparticle size. The pseudo-ternary system was composed of castor oil as oily phase, Brij O10 and 1,2-hexanediol as surfactant and co-surfactant (1:1), respectively, the aqueous phases are made up of the aqueous leaf extract of *Cnidoscolus chayamansa*, also known as Chaya Maya and a gold(III) chloride solution as metallic precursor. The aqueous leaf extract of Chaya Maya (CME) was employed as a reducing agent during synthesis. Different biological methods have been studied for the synthesis of metallic nanoparticles (MNPs) with the aim of replacing chemical reductants, which are usually highly toxic. The use of plant extracts is one of the most promising techniques due to the abundance of plants, efficiency, and ease with which MNPs can be obtained [1]. In this work, an endemic plant of Mexico recognized in the traditional Mayan diet for its great nutritional content, has been chosen, which has been previously studied in obtaining silver nanoparticles [2]. However, the high polydispersity in shapes and sizes and the low control over the particles formed are the main disadvantages in direct synthesis with natural extracts [3]. To control the formation and limit the growth of MNPs, the μE and nE systems described above have been used, just varying the composition of the system [4]. It is important to highlight that the components of the system are used in cosmetic applications and in formulations for daily use, so can be considered as a low toxicity system. The wide monophasic zone allowed the formulation of O/W and bicontinuous type microstructures that require a minimum amount of oily phase and were prepared by low-energy methods. The results indicated that the size of the AuNPs obtained was defined by the composition and nature of the system. The average nanoparticle sizes were in the range of 19 to 40 nm and the morphology was mainly polyhedral. In addition, it was obtained that the system provided a high stability to the colloidal gold solutions. A phasic behavior study of the pseudo-ternary system was carried out and the AuNPs were characterized by UV-vis spectroscopy (following the surface plasmon resonance band), DLS, STEM and Z potential. The proposed synthesis method is a simple methodology that can be carried out under mild reaction conditions and with low toxicity.

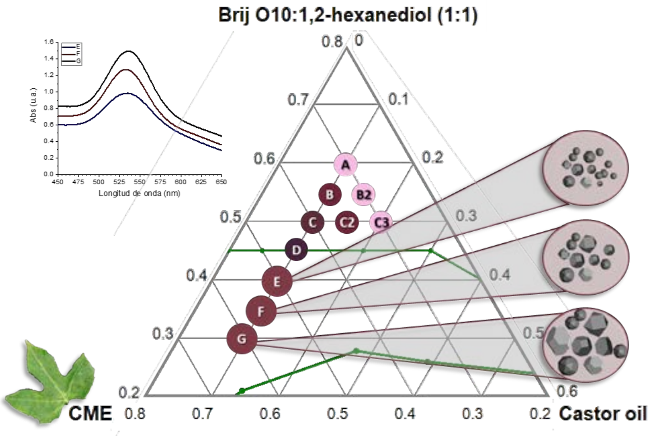

Fig 1. Graphical abstract of the AuNPs synthesis.

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New Generation Sustainable Polymers, Networks and Composites

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Polymers and polymer composites have been shaping modern daily life from aviation to consumable products. For material class with variety of properties utilized in a wide range of applications, it is natural that formulation science enabled such diversity. However, fossil-based polymer industry is facing many challenges which are mainly attributed to sustainability. It is now time to redesign majority of formulations via green chemistry principles to generate a polymer industry which addresses sustainability concerns.

Monomers obtained from renewable resources must possess significant properties and bear functionality for potential scale-up operations. I will show our efforts to polymerize mevalonic lactone methacrylate, partially biobased monomer, and how polymers having lactone units in the backbone can be highly functional.[1] Additionally, valerolactone-based vinyl monomer and its polymerization under fully green conditions will be elucidated.[2]

Introducing photoactivity to polymers via sustainable metal-free semiconductor (graphitic carbon nitride) offers unprecedented opportunities. Such systems can be highly attractive colloidal systems to obtain photoactive/photoinitiated polymers through dispersion formulations.[3]

Additionally, sustainable composite materials will be exhibited. Efforts to obtain sustainable benzoxazine-based carbon fiber composites suitable for aerospace applications will be shown. Last, sustainable epoxy based carbon fiber composites and formulations to introduce recyclability will be discussed.[4]

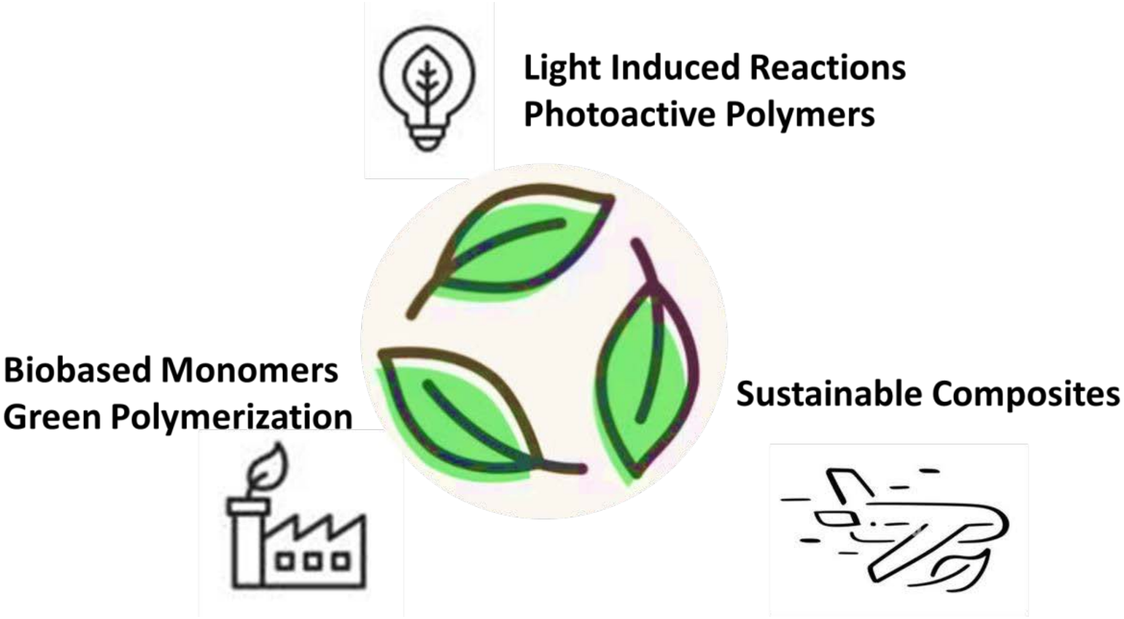

Figure 1. Schematic illustration of the submitted talk.

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Formulating nematic “tissues” of weakly bound discotic aggregates of carboxylate extended surfactants

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The general surfactant packing model considering spontaneous and effective packing by Ninham and coworkers and the first predictive thermodynamic modelling of Tanford, considering different hydrated aggregate shapes and the solvent containing monomers as pseudo-phases pseudo-phases with identic chemical potentials[1], the manifold of behavior of micelles and microemulsions structure was explained by shape transitions and the corresponding phase diagram, globular and giant micelles near lyotropic liquid crystalline phases.

While thousands of papers were describing extended surfactants phase diagrams and formulations based on them, microstructure and usage in formulations surfactants such as $C_{2i}Ei$ or $C_{2i}E_iCOONa$, the case of extended surfactants of generic formula C_iE_iCOOH or C_iE_iCOONa. had not been considered before to our best knowledge. It turned out that these micelles have a head-group so large that the commonly observed sphere to cylinder transition does not occur. A new type of nematic phase as well as a “direct”, i.e. o/w micelle without any bulk aqueous solution could be observed and understood [2,3].

This unusual behavior could be understood considering that carboxylate groups dispersed in hydrated ethoxy can be considered as the origin of a weak ($2K_bT$= 5kJ/mol) long range interaction (LRI) of up to 0.4 nm with some directionality. Instead of the classical interaction potential between micelles, 10 to 200 micelles can form tissues of more than 50 nm as prolate or oblate ellipsoids. By analogy to Metallic-Organic- Frameworks (MOF°, the road to Micellar-Metallic Frameworks (MMF) is open.

In this talk we will focus on some formulation of MMF’s useful in applications.

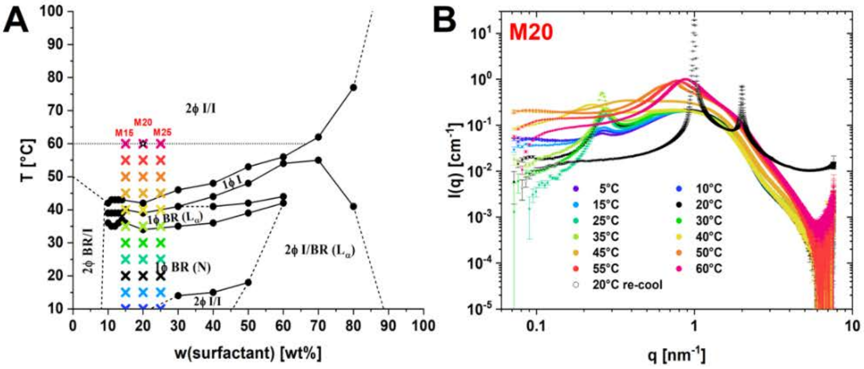

Fig 1. (left): the binary phase diagram of mixed extended single chain carboxylates surfactant in water I/ is liq-gas transition (N) for nematic gel and La for lamellar phase (right): the scattering on absolute scale of a nematic phase with 20% active matter in its three possible states: nematic till 35C, water-poor o/w micelles (L*) above 35C and lamellar phases (in black: after re-cooling)

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Valorization of lignins as sustainable multifunctional ingredients for cosmetic formulations

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Formulating with plant-based instead of petroleum-based ingredients while keeping the same performances has gained much interest in the cosmetics industry and many recent progresses have been made. Nevertheless, despite a lot of researches in this field, only few have been dedicated to biomass waste recycling although the growing availability of lignocellulosic biomass leads to the emergence of a biosourced chemical industry that may highly compete with petrochemicals. Lignins are polyphenolic polymers and represent the most abundant source of nonsaccharidic biopolymers in plant biomass with 30% of organic matter in the biosphere [1]. Despite their high industrial availability from paper industries and biorefineries, they remain poorly valorized because of their complex chemical structure (Fig 1.A), high molecular mass and polydispersity combined with low solubility in commonly used solvents. Lignins represent a good alternative to propose sustainable multifunctional ingredients in fields such as cosmetics by exploiting their different physico-chemical properties, such as antioxidant [2], anti-UV [3], antimicrobial [4] and interfacial properties [5].

The challenge of the present work is to conceive a strategy to incorporate lignins within formulations in order to achieve interfacial stabilization. Therefore, to obtain more soluble fractions with less structural heterogeneity and modified interfacial properties, an industrial lignins fractionation process was designed followed by the modification of their structure by functionalization with apolar moieties derived from biosourced fatty esters. We demonstrated that both lignins structure and corresponding pH solutions were important for their emulsifying properties. For the first time, an innovative strategy was developed to formulate lignins in simple O/W emulsions for soft matter systems such as cosmetic formulations (Fig 1.B). The present study unambiguously brings promising results for the valorization of lignins as a natural resource to conceive new multifunctional biobased emulsifiers with promising biological properties for industrial applications including cosmetics.

Further studies will focus on targeting other functionalities and properties of lignins for cosmetic applications.

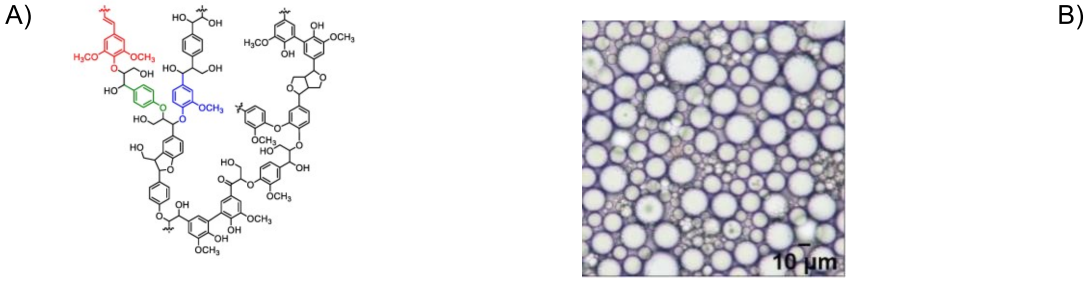

Fig 1: A) Schematic representation of lignins structure reproduced from [6], B) Optical microscopy of lignins O/W emulsion (G x 400, scale bar 10 µm)

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Preparation of robust carbon monoliths derived from phenolic resin for CO_2 separation

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In recent years, biogas upgrading processes have gained increased attention due to depletion of conventional fossil fuels and increasing targets for renewable energy sources. However, these processes require energy-efficient methods for CO2/CH4 separation to increase the calorific value and marketability of the biogas. In this context, porous carbons materials from phenolic resins appear as an attractive alternative for selective capture and separation of CO_2 [1]. Thermoplastic phenolic resins are interesting materials for the preparation of different porous carbon forms and they can be synthetized by polymerization of phenols and aldehydes [2]. Preparation of porous carbons via carbonization of phenolic resin materials offers several advantages: high char yield, chemical stability, thermal stability, high surface area, high CO_2 adsorption selectivity and capacity [1,3].Taking the above into account, the main purpose of this study is to develop porous carbon monoliths from resol-type phenol–formaldehyde resin and enhance its performance (especially CO_2 adsorption and specific surface area) by optimizing the pyrolysis and activation processes. The effect of the amount of hexamethylenetetramine (HMTA), used as crosslinker in the synthesis of the phenolic resin) on the CO_2 adsorption performance was also investigated. For this purpose, the carbonized material obtained are characterized using different analytical techniques, including elemental analysis (CHNS), measurement of N_2 (BET surface) and CO_2 sorption isotherms (microporous surface, adsorption capacity), SEM, TEM, etc.

Results: Figure 1 provides an overview of the visual appearance of the material after each stage of the experimental procedure. It also shows CO_2 adsorption isotherms of the obtained carbonized materials. Table 1 illustrates the main results obtained (CHNS, microporous surface, and CO_2 adsorption capacity). These results reveal that the carbon monoliths show good CO_2 adsorption capacity compared to results found in the literature [1-3]. Additionally, there is a slight increment of CO_2 absorption capacity when the HMTA content is increased in the resin. In the same way, the carbonized material presents a higher char yield and a higher surface area, which is relevant for efficient CO_2 adsorption applications

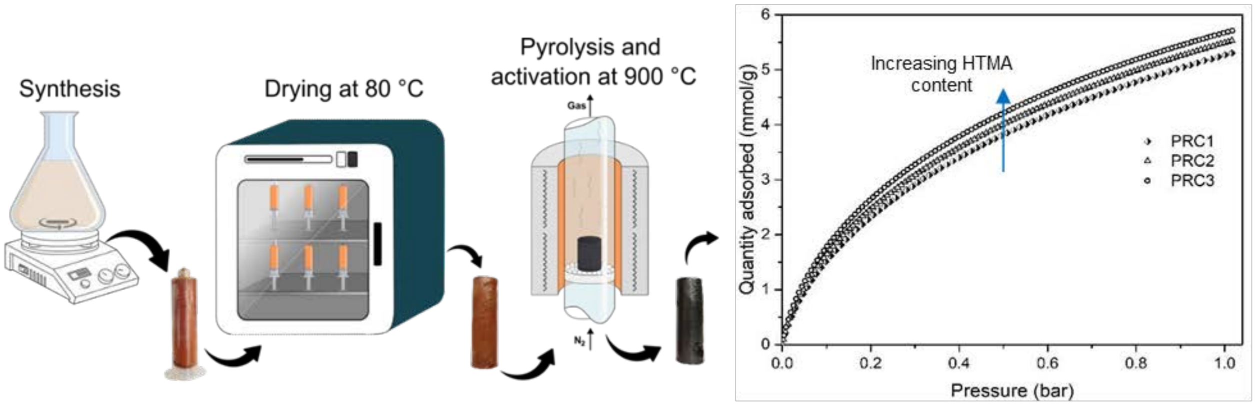

Fig 1. Schematic design forporous carbon monolith fromsynthesis of phenolic resins

Sample	HMTA (g)	Elemental analysis			Char yield (%)	Micropore surface area (m^2/g)	Quantity Adsorbed (mmol/g) at 0°C and 1 bar
		%N	%C	%H			
PRC1	0.08	0.68	96.06	0.37	41	905	5.36
PRC2	0.12	0.70	95.75	0.40	41	927	5.58
PRC3	0.16	0.88	95.65	0.37	42	942	5.77

Table 1. Textural properties and elemental analysis of the porous carbons. [a] from activated material

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Development of new lipopeptide green surfactants from silk sericin

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The production of environmentally sustainable amphiphilic molecules constitutes one of the major issues of the surfactant industry, because of the pressure from regulatory legislation and growing consumer trend towards environmentally-friendly chemicals. Natural-based surfactants are mainly produced from agricultural food biomass such as sugars, starches, vegetable proteins and oils. However, these high-quality fractions of biomass are in competition with food and feed industries, which gives rise to ethical, environmental and political concerns due to the rapid growth of the world population[1]. In this context, the development of new eco-friendly surfactants, derived from non-food silk proteins can represent an important challenge. Silks derived from silkworms are composed of two fractions: fibroin (~70%) used in textile industry, and sericin (~30%) removed by the degumming process during silk fibers production[2,3]. Sericin is an undervalued protein, which use in the development of amphiphilic molecules has been little studied to date.

The main goal of this study is to develop an original way for silk sericin valorization to produce lipopeptide amphiphiles and to evaluate their adsorption properties. The first step involves the separation of sericin and fibroin fractions[4]. Then, sericin peptides are obtained by enzymatic hydrolysis. Finally, the grafting of hydrophobic functions on peptides *via* primary amino groups is performed. For this last step two methods of peptide functionalization were studied: conventional Schotten-Baumann acylation with fatty acid chloride in aqueous medium, largely applied on industrial scale, and new alternative approach using mechanochemical methodology for fatty acid grafting in solventless conditions. The surface activity and self-organization of obtained lipopeptides were investigated by surface tension measurements (Fig 1).

Results obtained showed that sericin can be successfully hydrolyzed using Alcalase enzyme with the hydrolysis degree (DH) between 20 and 50%. The grafting of hydrophobic chain of various length (C_{10}, C_{12}, C_{14}) to sericin peptides by conventional method was performed with acylation rate (ratio of grafted terminal *N*-functions) from 27 to 42%. Overall, the acylation rate was not significantly influenced by fatty acid chain length. Moreover, the results of solvent-free grafting of fatty acid on sericin peptides by mechanochemistry showed very promising results with comparable rate of functionalization. Lipopeptides produced from silk sericin showed good surface-active properties with significant lowering of water surface tension and the existence of a critical concentration for micelle formation.

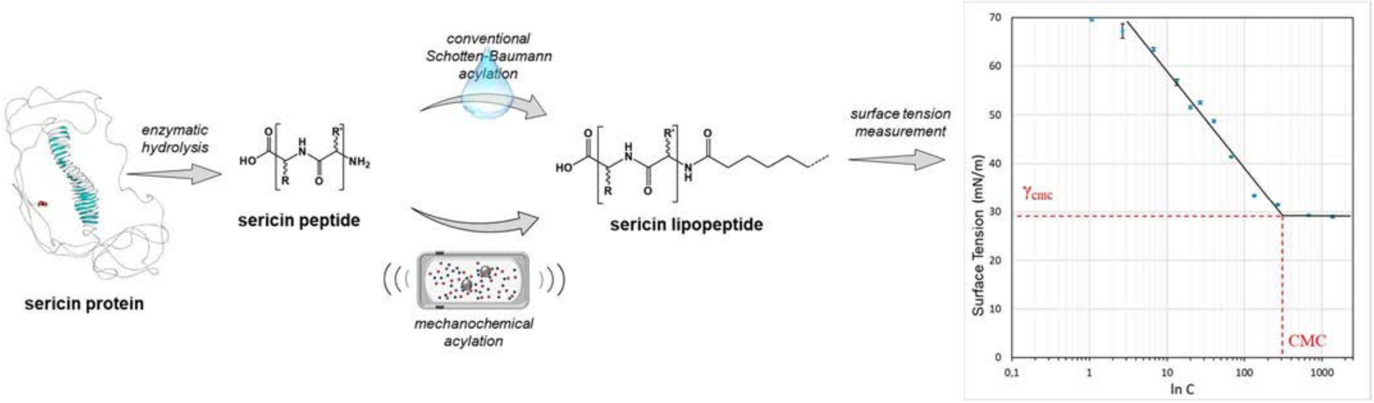

Fig 1. Methodology used for silk sericin-based lipopeptides' production

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Formulating nanostructured soft particles from a technical-grade diglycerol surfactant

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Glycerol-based surfactants find applications in many fields of industry. They are usually available as a complex mixture of mono-, di-, tri, and tetraalkyl esters and their respective isomers

Herein, we report on the formulation of nanostructured soft particles, i.e. hexosomes, from a technical grade diglycerol surfactant, namely, technical diglycerol isostearate. The as-received surfactant forms a reverse hexagonal liquid crystal that is stable up to 70ºC. Hexosomes were produced by an emulsification/evaporation method using a block copolymer as dispersant; the internal structure of hexosomes was confirmed by SAXS and Cryo TEM. A model drug

(ketoprofen) was encapsulated in the formulated hexosomes and a pH-responsive release behavior was demonstrated [1].

In order to better understand hexosome formation, the technical grade sample was separated into three fractions: unreacted glycerol, monoester and a mixture of components with higher esterification degree. It was found that glycerol prevents the formation of a single-phase hexagonal liquid crystal. In contrast, the monoester fraction produces thermotropic and lyotropic lamellar phases. The presence of higher esterification degree components induces a lamellar-reverse hexagonal transition. The collected information on phase behavior can be used to rationally formulate vesicles or hexosomes [2].

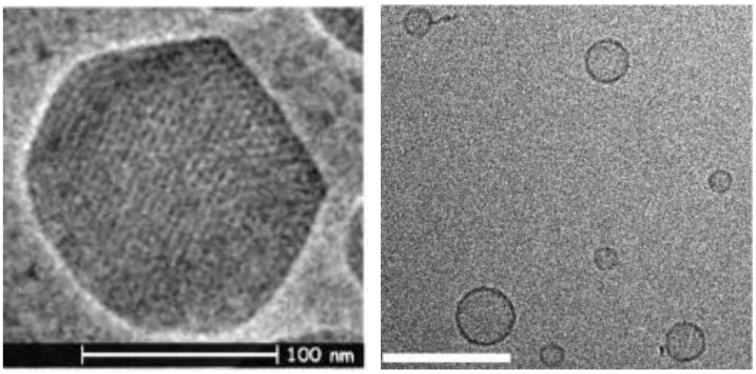

Fig 1. Cryo TEM images of hexosomes (left) and vesicles (right) prepared from the technical grade diglycerol surfactant

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How Microbicidal efficacy of Chemical Disinfectant product are evaluated currently in European? What will be the next steps needed to adapt to new Sustainable challenges? General overview proposed.

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Bio-cleaning and disinfection are key elements of infection prevention in healthcare settings but also in pharmaceutical industry of Food industry. However, each field encounters its own difficulties depending on the resident microbial ecology and direct environment. To this is added antibiotic/antifungal resistance, which is currently adding a pressure of selection of microbial strains in specific environments. Pandemic situations such as COVID-19 are reinforcing the essential need for infection control that health services require.

One of the basic answers is the use of chemical disinfectant detergent products in line with the hygienic protocols in force. Chemical detergent-disinfectant products in Europe are subject to medical device and/or biocidal regulations. The microbiological efficacy of the products is then evaluated according to the European standards established by the European standardization commission CEN/TC 216 (European Commission for Standardization / Technical Committee 216).

This European Commission is led by public and private actors from European member countries. It is important to note that the normative dynamic continues to evolve over the years to provide effective means of control to the challenges encountered at the level of institutions.
The objective of this communication is to present the current normative developments in the field of disinfection and explain the European standards necessary to evaluate the efficacy against a range spectrum of microorganisms of chemical disinfectant products.

The evolution of those European standards requires, on one hand, to exchange as much as possible between public actors and Chemical manufacturers of products but also with researchers to be able to integrate new technology that could improve the reproducibility and repeatability of laboratory tests when these European standards are produced. On the other hands, European Standards designed to evaluate Microbicidal efficacy of Chemical products also need to adapt to new concept of Today formulation that fall within sustainability development.

Hydrogels based on functional hyperbranched polyglycerols

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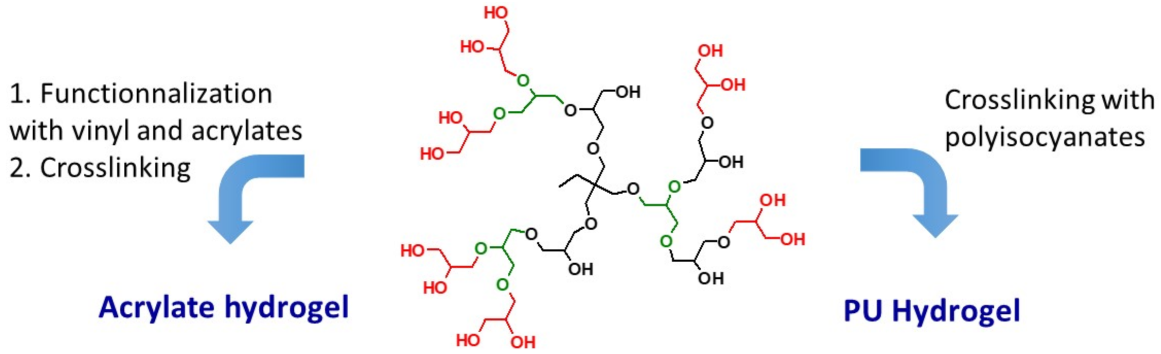
In this work, we will present the versatility of hyperbranched polyglycerols (HPG) that can be implemented according to different chemical processes to prepare polymeric networks used for the development of new hydrogel materials. The first process involves the controlled functionalization of the OH terminal groups of hyperbranched polyglycerol by maleic, itaconic and (meth)acrylic polymerizable groups. Such polymerizable groups are co-polymerized with selected (meth)acrylates in order to prepare crosslinked materials. The influence of the functionalized HPG content and of its functionality (namely average number of functional groups / macromolecule) on swelling properties and mechanical properties has been investigated and will be displayed. Since hyperbranched polyglycerols also display numerous OH end groups, they can be considered as a good candidate as macro-crosslinker in polyurethane chemistry, especially when reacted with various molecular and oligomeric polyisocyanates, leading to polyurethanes water swellable networks. In this part, we will present the influence of the structural parameters (HPG MW, nature, MW and functionality of polyisocyanates).



Formulation of molecular hydro-organogels based on modified aminoacids. Effect of chemical structure on gelation kinetics and thermoreversibility

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Hydrogels find numerous applications in formulated products. Their rheological properties lead to liquid-like or solidlike mechanical behaviour according to external stress and allow reaching targeted performances in operating conditions. Physical hydrogels rely on molecules or/and macromolecules interacting through low energy interactions (e.g. hydrogen bonds) and on physical entanglements between supra- or macromolecular species. Improving the control of the rheological properties requires more insight about the links between the molecular/supramolecular scale and the macroscopic physical properties. Thus it is of primary interest to characterize such hydrogels by combining spectroscopic and rheological techniques.

In that work, a natural aminoacid, lysine, has been chemically modified for synthesizing three gelating compounds with similar structures and differing from each other by one or two functional groups. All three molecules were fully soluble in dimethylsulfoxide (DMSO) and gelled DMSO/H_2O mixtures with various compositions. Hydrogels could be produced by following a specific formulation procedure involving dialysis of previously prepared DMSO/H_2O gels.

Mechanical strength of the gels, thermal/mechanical reversibility, temperature of gel-sol transition as well as kinetics of gel formation were correlated to the chemical structure of the gelators as well as to the composition of solvent. Subtle variations in the chemical structure of the gelator dramatically modified some properties like the time for gel formation (which varied between 10 and 5000 s) or thermal reversibility.

The formulation pathway had to be adapted to the gelling behaviour of each molecule. In addition a specific geometry was designed for rheological measurements[1]. To get insight in the association phenomena and the structural characteristics of physical gels, we combined the use of rheology and spectroscopic techniques like infrared and Raman spectroscopy. The transient formation of gel was modeled using empirical equations and correlated to stationary rheological properties[1,2].

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Formulation and characterization of thermosensitive Hydrogels based on Cellulose and Xyloglucan.

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The Plant cell wall is a very commonly used system as a source of inspiration for understanding hydrogel systems. Indeed, it's composed of cellulose, hemicellulose and pectin. These compounds form a complex swollen network that can be described as a hydrogel. Cellulose is closely associated with hemicelluloses, for example Xyloglucan, which gives the wall amazing mechanical properties[1]. In this context, we are interested in the formulation of CelluloseXyloglucan hydrogels with the objective of formulating materials with high-performance physicochemical and mechanical properties. We will benefit from enzymatic tools such as the presence of the enzyme "β-galactosidase" to obtain hydrogels with thermosensitive properties[2]. A phase diagram has been developed to identify the different CNCXG systems. We were able to observe between liquid systems, weak gels, strong gels and thermosensitive gels. The liquid-gel phase transition was observed at XG/CNC, XG-DG/CNC ratios greater than that required for full CNC recovery. This increase is probably due to the effective hydrodynamic volume of CNCs due to the formation of XGCNC complexes. Concentrated hydrogels were developed by dialysis in a 5% PEG solution[3]. The mechanical properties of the systems were evaluated by rheology. The microscopic evaluations were correlated with the viscoelastic moduli (G', G''). Thermosensitive hydrogels have been observed with a reversible thermal transition that varies between 35 and 40 °C depending on the concentration. This thermal reversibility offers the possibility of applying these systems in various application, particularly in the biomedical field.

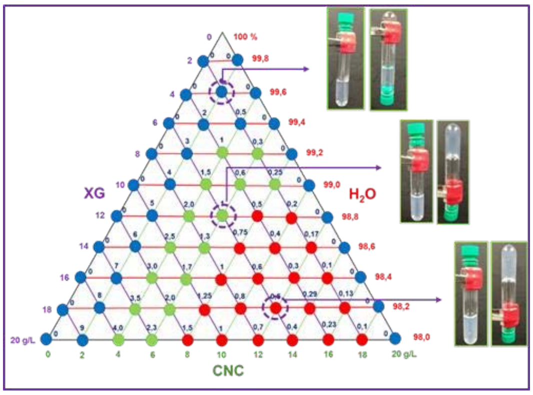

Fig 1. Phase diagram for identification of different CNC-XG systems.

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Self-assembly behavior in systems containing alkyl imidodipropionate and glutamate diacetate

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Industrial applications of water-based surfactant systems often require the use of chelating agents to deal with water hardness. Nevertheless, including chelating agents reduces surfactant solubility. The opposite behavior has been observed for amphoteric surfactants, allowing the formulation of concentrated systems.

In the present research the physicochemical properties of solutions containing imidodipropionate based surfactants and glutamate diacetate chelating agent have been investigated. Interactions between the chelating agent and the amphoteric surfactant were monitored by nuclear magnetic resonance (NMR) at different concentrations, while the macroscopic properties, such as viscosity and cloud point (CP), were evaluated in presence of a non-water-soluble alkyl ethoxylated surfactant.

When the concentration in chelating increased, the viscosity and CP passed through minimal and maximum values, respectively. These results seem to indicate that there are changes in micellar shape or size when amphoteric surfactants are used as solubilizers in nonionic/chelate systems. The reduction in viscosity and the increased surfactant solubility suggest that the interaction between chelating agent and amphoteric surfactant increases the size of the hydrophilic head group of the surfactant. This interaction was further demonstrated with NMR. We hypothesize that these interactions promote the formation of smaller, more spherical micelles at the origin of these inflection points. For concentration above, the reduction in cloud point, and the increase in viscosity could be explained by the salting-out effect, since increased concentrations of glutamate diacetate results in higher ionic strength and pH.

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Interactions at the interface of gelled-oil nanoparticles in water: from dispersions to colloidal hydrogels

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The cosmetic industry is always looking for new textures for topical products. Indeed, such formulations require adequate hardness and consistency to be efficiently spread on the skin and to offer a pleasant sensory experience. To this end, research constantly develops new formulations, inspired by emulsions. This work focuses on an innovative family of organogel particles, which can be used as a vehicle for active ingredients [1], and its potential use for topical application. The main objective of this work is then to modulate and understand the texture and applicative properties of these systems.

The preparation process of these gelled-oil nanoparticles is based on the sol-gel phase transition of the organogel. They are obtained by hot emulsification ($T>T_{gel}$) in presence of an aqueous solution of stabilizing agent, resulting in a stable semi-solid dispersion after cooling ($T<T_{gel}$).

Different dispersions of organogel particles were prepared, leading to a large range of interesting textures, from liquid dispersions to structured gels [2]. The study of their properties, depending on ingredients natures and ratios, highlighted a key role of the oil polarity in their texture. Electron microscopic observation, associated to interfacial tensions analyses, proved that the occurring structuration results from ingredients interactions at the interface of the initially dispersed particles, forming a colloidal hydrogel.

These results enable the understanding of the mechanisms leading to different particles organizations, and thus a control on the texture appearance of the systems through formulation.

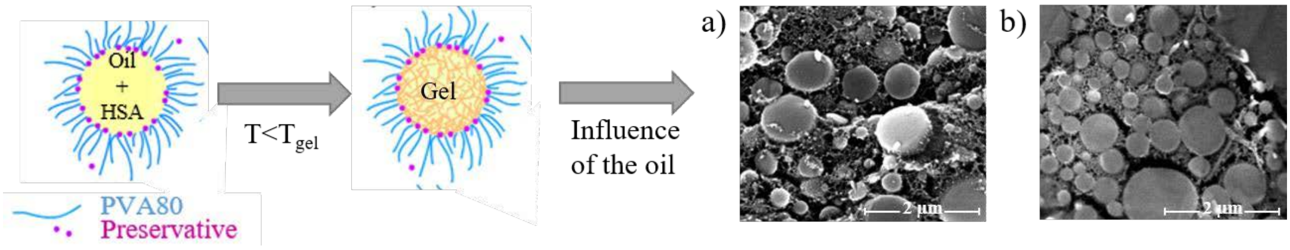

Fig 1. Schematic representation of nanoparticles gelation, leading to a) a stable dispersion, or b) a colloidal hydrogel, depending on the nature of the oil.

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Science-based formulation via webapps

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The predictive formulation science, Hansen Similarity Parameters (HSP) and Hydrophilic Lipophilic Difference (HLD), are very powerful tools to match, replace and compatibilize ingredients, resulting in maximum overall performance of end-products, while minimizing development time. These models are applicable to solutions, dispersions and emulsions, and give a predictive parameter to a wide variety of ingredients, applicable to develop coatings, inks, personal and home care, etc. Each ingredient parameter can be used repeatedly and it drastically reduce experimental work, time and costs, which makes it a more sustainable R&D workflow. VLCI established the world's largest shared HSP and HLD dataset of commercial ingredients, which is linked to our science-based formulation web-apps to visualize and perform searches based on calculations. The collaborative framework of the platform allows to add and share ingredient parameters, when needed, while securing each users own private datasets, formulations and IP. Both HSP and HLD theories and platforms will be presented, including examples of assisted final product formulations in different fields, as well as how this can boost formulation R&D.

NMR relaxometry: a tool to probe complex formulations

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Nuclear magnetic resonance (NMR) due to its weak interaction with the sample is a non-invasive tool perfectly suited to probe complex formulations. In addition to the spectroscopic part of the technique, a wealth of information can also be accessed when the way the magnetic information is lost, i.e. the relaxation, is investigated. NMR relaxation is caused by the molecular fluctuations of the spins, it is then a particularly efficient witness of the molecular dynamics and interactions in dispersed systems. For instance, the sensitivity of the solvent relaxation to surfaces makes it a valuable tool to test the specificity or the accessibility of surfaces to the solvent molecules. This specificity was used in the pioneering works of Cosgrove[1] to probe the surface state and assess the polymer adsorption on dispersed silica nanoparticles.

Since then, recent efforts were focused on the stability on proteins in solutions in the framework of pharmaceutical preparation[2]. It was shown that the transverse relaxation due to the is more sensitive to the aggregation processes than the longitudinal relaxation[3]. The origin of the effect comes from the differing frequency dependence of these two relaxation pathways that we will comment in details.

To go further, one can consider measuring the frequency dispersion of the relaxation rate to have access to a wider dynamic picture of the molecular dynamics in the sample. This is actually made possible thanks to the fast field cycling (FFC) technique that can explore a Larmor frequency range between a few kHz up to a few tens of MHz. The use of this technique allows to determine specifically the different nature of surface exposed to the solvent in aqueous pigment dispersions of green earth phyllosilicates[4]. Finally, it can also give access to the complex interaction between an egg yolk binder and the green earth pigment in a reformulated ancient paint[5].

NMR relaxation dispersion is then an unrivaled tool to investigate complex formulations via the dynamics of the solvent.

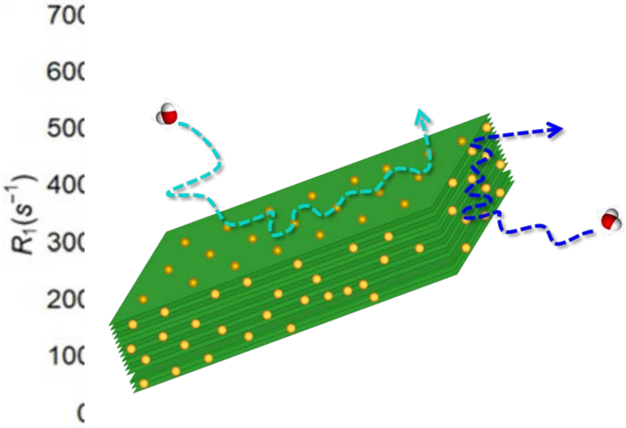

Fig 1. Contribution of the basal and edge surfaces of a green earth phyllosilicate pigment to the dispersion of solvent NMR longitudinal relaxation[4]

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NMR kinetic monitoring of the cutting fluid organic waste's hydrolysis all along the immobilization in alkali-activated materials

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Geopolymers (GP) are synthetic inorganic aluminosilicate cements that are formulated at room temperature by activating a precursor solid in alkaline conditions. Recently, the immobilization of organic liquids (OL) into GP has been successfully applied to nuclear waste, where the OL is permanently confined in the form of micrometric droplets. One type of OL that is commonly found in nuclear waste is cutting fluids, which currently have no direct treatment route. In this study, the immobilization of cutting fluids into GP is investigated.

Cutting fluids are typically emulsions of OL in water – with various additive depending on the specifications of the cutting operation – and eco-friendly cutting fluids are often made of vegetable oils, which are triglycerides. When these oils are immobilized in GP under highly alkaline conditions, saponification reactions are thought to occur, transforming the triglycerides into carboxylates and glycerol. On one hand, the fatty acid soaps produced by this reaction act as surfactants, making it easier to immobilize the OL by dispersing it in small droplets within the GP matrix. On the other hand, the division of a molecule with a high molecular size into smaller molecules promotes the phenomenon of leaching and the diffusion of these molecules outside of the matrix.

The saponification kinetics in a GP environment are studied in this research using Nuclear Magnetic Resonance (^{1}H NMR) Spectroscopy. Sunflower oil is initially hydrolyzed in a typical GP porewater composition, and the resulting saponification products are quantified, with a focus on glycerol and fatty acid soaps [1]. The study finds that saponification is almost complete, with only small amounts of by-products present (Figure 2). During the geopolymerization, the silicate species present in the activating solution act as "hydroxide reservoirs", and progressively release the hydroxide ions during the condensation of aluminosilicate species [2].

Therefore, 29Si NMR investigates the structures changes of silicate species during the geopolymerization, in order to evaluate the effect of the saponification reaction.

The research also investigates the incorporation of a commercial cutting oil into GP, to determine how saponification reactions occur and whether they modify the cutting oil composition. The study seeks to identify mobile components of the cutting oil within the GP porewater and to explore means of retaining them within the GP.

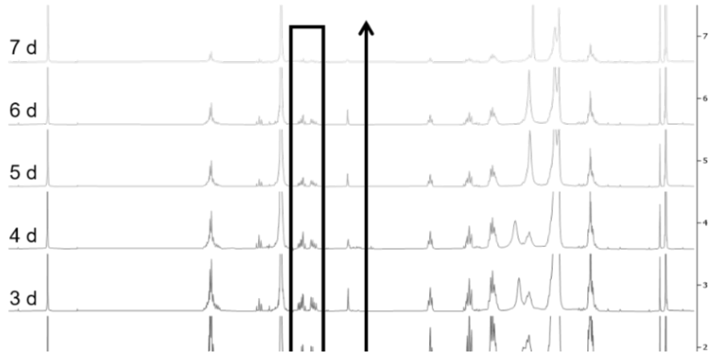

Figure 2. ^{1}H NMR evolution of the saponification of vegetable oil in alkaline medium (the boxed peaks correspond to the glycerol unit of the triglycerides)

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Natural gums in complex formulations: molecular characterization by mass spectrometry

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Natural gums are viscous water-soluble substances, originating from higher plants or fermenting bacteria. The adhesive, emulsifying and stabilizing properties of gums widened their use in many applications, notably in the field of agro-food, of pharmaceuticals and cosmetics as well as of cultural heritage. In fact, natural gums constitute an important, natural and safe ingredient in the formulation of sauces, creams, gels, watercolors, inks and gouaches. Structurally, they are proteoglycans with a small but significant amount of protein (1-6%), with a predominance of polysaccharides (94-99%). Natural gums' structure depends on the producing species and environmental conditions. Their structural and chemical modifications characterization is crucial to identify the gums, providing valuable information about the products formulation. We developed an original workflow to characterize the natural gums involved in the formulation of various types of products. This one-pot workflow consists of implementing two successive enzymatic digestion steps in a centrifugal filter. The first step is dedicated to polysaccharides digestion with galactanase and/or mannanase for plant-derived natural gums, and cellulase for bacteria-derived natural gums, while the second is a tryptic digestion of proteins into peptides. This method makes it possible to obtain fragments of oligosaccharides and peptides separately. MALDI-FT-ICR MS analysis following in situ derivatization with the 3aminoquinoline allows oligosaccharide fingerprinting of the natural gums. In addition, chemical derivatization with reductive amination by ABBE (p-aminobenzoic acid butyl ester) and by nanoESI nanoLC-MS/MS analysis with high sensitivity and resolution was carried out in order to gather detailed structural information on these oligosaccharides. Peptides analysis by nanoESI nanoLC-MS/MS allows the identification of proteins and therefore the originating species of the natural gums. We started by optimizing the workflow with commercial natural gums. Subsequently, we applied it to characterize natural gums in industrial complex formulations, such as sauces, plant milks, cosmetic products, as well as watercolors.

Numerical prediction of long-term stability of liquid formulations determined by visual observation and Static Multiple Light Scattering

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The demonstration of long-term stability is a key step when developing liquid formulation as it has a major impact on product shelf life, transport, and its final end-use properties. Long-term stability is often determined visually using the classical bottle test. However, this method is often not compatible with current product manufacturing process which requires rapid development and large screening of formulations. In this view, Static Multiple Light Scattering (SMLS) analysis has been widely used to detect instabilities at an early stage compared to visual observation. In this study, we developed a numerical predictive algorithm to evaluate the stability time (*i.e.* time of first instabilities appearance) determined by naked eye and SMLS. This predictive algorithm was built on the analysis of several tens of liquid formulations with carefully controlled properties using a camera setup and SMLS analysis. The camera setup mimicked the human vision by recording images of the sample at a given frequency. Image processing combining edge detection with criteria on contrast and size was applied to these sequences of images to evaluate the naked eye stability time objectively. This stability time was also evaluated using SMLS measurements by imposing a monotone and minimal transmission or backscattered intensity conditions. As part of these experimental results, a numerical model was built to simulate the time and space resolved SMLS profiles according to initial formulation parameters (densities, viscosity, refractive indexes, size distribution). The predictive algorithm was developed by correlating these simulations of time and space resolved SMLS profiles to the stability time measured experimentally with the camera setup and the SMLS technique. This predictive algorithm was also tested on non-controlled emulsions and solid dispersions proving its applicability to more realistic systems. According to this validation, this algorithm appears to be a major step toward the rapid screening of long-term stability of liquid formulations, with applicability in various industrial field dealing with formulation shelf life (cosmetics, pharmaceutics, food & beverages, paints & inks, …etc.).

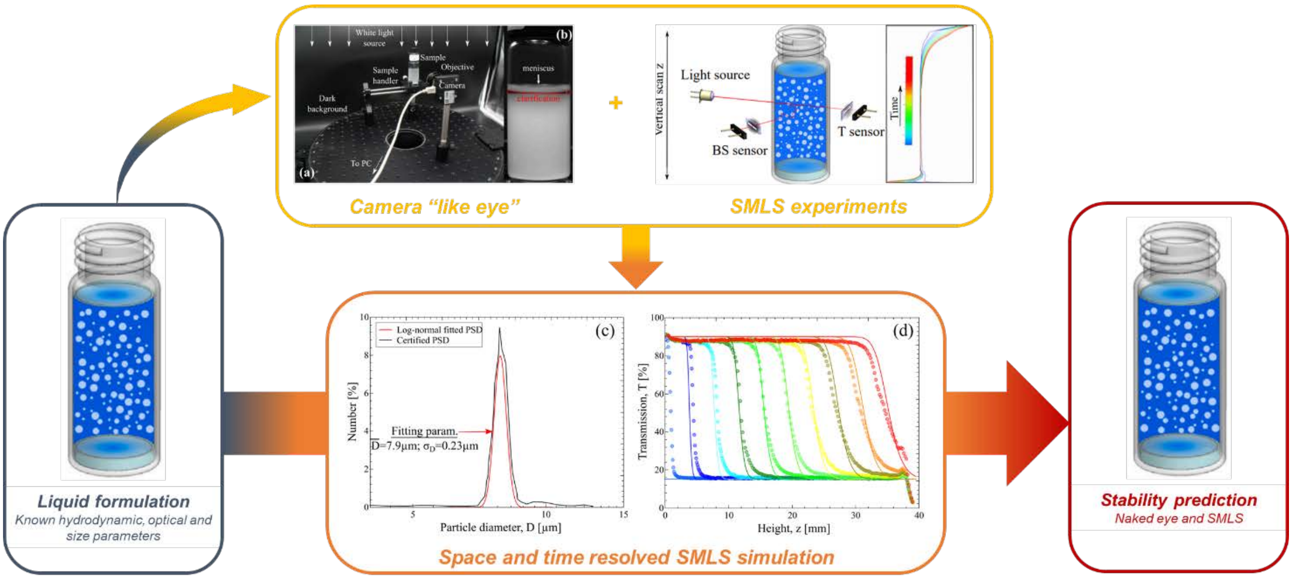

Fig 1. Schematic strategy for predicting long-term stability of formulations [1]

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Thermal profiling with DWS to accelerate development from raw materials to finished

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The development of new cosmetics is a complex process. Especially, when using lipids and fatty compounds, many aspects must be studied, starting from the compatibility of the ingredients to the overall stability. process problems. In most of cases, these issues are due to the thermal behavior during heating and cooling. Customers may observe exudation spots, recrystallization, or other visible defaults. The detection of these issues is complicated, especially in the case of solid and semi-solid cosmetics, where the quality issue appears only after months. It is therefore of utmost interest for the developer to be able to evaluate a formulation as soon as possible.

Recently, a highly sensitive technique to control microstructure mobility - Diffusing Wave Spectroscopy (DWS) [1, 2, 3] – was combined with accurate temperature control. Samples can be analyzed during heating and cooling ramps to obtain phase transition temperatures (melting point, crystallization point, pour point, …). These results are primordial to understanding the impact of pure and mixed waxes and avoiding problems during preparation and process.

Moreover, the instrument allows programming temperature cycles (typically 6 to 10 complete cycles between 4°C and 40°C) to imitate the thermal stress a cosmetic product undergoes during its life cycle. These accelerated stability tests allow us to screen samples and evaluate stability as a function of the response to the cycles. An equal response indicates a stable sample, and a decreasing response indicates instability. Thus, a measurement of several hours can indicate a stable or unstable formulation and decrease the development time significantly.

This work will show several examples, of how an innovative measurement method can help to choose the right raw materials as a function of melting point and purity. Control its compatibility with other compounds in the formulation. Finally, a method to study lipstick stability is presented, that allows the evaluation of new formulas within a day.

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Advanced Dynamic Light Scattering and its Applications to Life Sciences

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Dynamic light scattering (DLS) is a powerful characterization technique routinely used in research and formulation development in life sciences. It provides a measure of the size of the particles in a suspension, as well as rapid aggregate detection or long-term stability monitoring. Its applications cover a wide range of life science systems such as nanocarriers, proteins, drug products or adjuvants.

While DLS is a well-established characterization technique that provides fast and in-situ information, it is still undergoing constant improvements. In particular, the notorious need for highly diluted samples has long been a major limitation in DLS.

In this context, we will introduce the Modulated 3D DLS technology, allowing to suppress multiple scattering directly in the DLS signal. The measurement of sample at any concentration is thus possible without any limitations.

The access to sizes below 5 nm is another well-known challenge that prevents, among other examples, the accurate characterization of DNA and its conformation changes. This difficulty can be overcome by a different, yet similar improvement of the detection system called the Pseudo-Cross Correlation technique.

This presentation will feature a review of the scientific fundamentals of DLS and introduce the technologies mentioned above.

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Meeting the challenge of better understanding the interfacial behavior of ingredients

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TECLIS Scientific

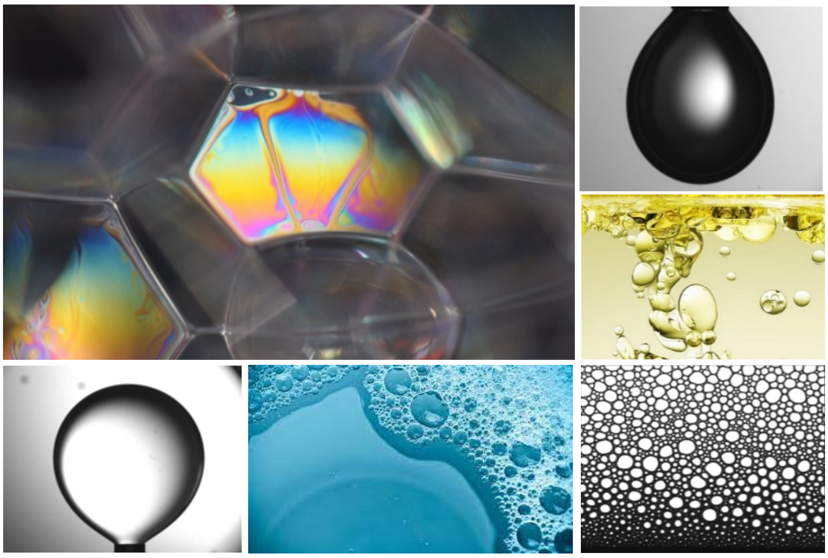
In many industries, the use of liquid foams offers numerous advantages. Foams are lightweight and easy to handle, they allow for the use of fewer raw materials for a fixed volume of the final product, and they possess interesting expansion properties. Foams are often desired in personal care products and food products. However, in other industries such as printing, pumping, and lubrication, foams are undesired, and anti-foaming agents are used. Additionally, many processes such as flotation and enhanced oil recovery utilize foams.

Therefore, it is crucial to be able to control a liquid foam and understand the phenomena responsible for its destabilization in order to optimize the formulation of foaming products and the industrial processes affected by foaming issues. Although most foam analyzers can accurately characterize the macroscopic properties of foams, the challenge of connecting macroscopic properties to the microscopic behavior of surfactants at the interface remains.

Foams, like emulsions, are characterized by an extremely high volume-to-surface ratio. This prevalence of interfaces in these divided materials suggests that interfaces may play a predominant role in the macroscopic properties of these systems. Interfacial tension is a parameter commonly used in the field of interface science to describe the affinity between two immiscible phases. It is argued that when surface tension decreases, surface energy decreases, and thus, the system requires less energy to exist and becomes more stable. However, this argument does not consider that the surface tension value is always positive, and therefore, the system can only tend towards an unstable state from a thermodynamic perspective. Surface tension alone cannot explain why a soapy solution and a hydroalcoholic solution, both having the same surface tension values, result in stable foam in the former case while the latter leads to a rapidly destabilizing bubbly liquid.

Since measuring surface tension is not sufficient to explain everything, we recommend a simple measurement protocol that leads to a more comprehensive characterization of the interface. This protocol combines dynamic surface tension, interfacial rheology, frequency and amplitude sweeps, and compression/dilatation of the interface. Through a few examples, we will demonstrate how these dynamic tension measurements can reveal interfacial behaviors such as the formation of solid membranes, the emergence of nonlinear regimes, and, in some cases, establish a connection with the molecular structure.

By demonstrating a better understanding of the interfacial behavior of ingredients, we can add value to the formulation process.



POSTERS

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P13	Antoine Simon, Justine Lamielle, Marlyatou Lassalle, Léonie Jourdain, Jesus F. Ontiveros, Véronique Nardello-Rataj	Influence of formulation, composition and process variables on the properties of organogel-based water-in-oil emulsions
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P15	Lucie Delforce, Jesús Fermín Ontiveros, Véronique Nardello-Rataj, Jean-Marie Aubry	Rational design of W/O nanoemulsions using the normalized HLD concept and the formulation-composition map

P16	Lucie Delforce, Evamaria Hoffmann, Véronique Nardello-Rataj, Jean-Marie Aubry	TiO_2 nanoparticle dispersions studied by sedimentation analysis: Hansen Parameters vs. DLVO interpretations
P17	Véronique Nardello-Rataj, Christel Pierlot, Jesus Fermin Ontiveros, Mike Ortega	HT-SMARTFORMU: A High Speed Formulation Technological Platform
P18	Xiaoyang Yue, Lianjie Wang, Mohammed Ahmar, Jesus Fermin Ontiveros, Véronique Nardello-Rataj, Yves Queneau	Innovation in biobased surfactants from carbohydrate-based furanic platform molecules
P19	Tounsi Mohamed Noemen, Aschi Adel, Kassab Ghaz	Characterization and analysis of some macromolecular compounds coated with essential oils
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P21	Blandine Boche, Soukaina Benoujja, Nicolas Huang, Bertrand Fournier	Influence of oil properties on Pickering emulsions stabilized by quercetin
P22	Akinori Fujita, Hironobu Matsueda, Masaaki Akamatsu, Kenichi Sakai, Hideki Sakai	Adsorption of Sulfur-Type Extreme-Pressure Agent
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P24	Jordan Bassetti, Hadjer Crevits, Christel Pierlot, Arnaud Poulesquen	Solid impregnation of organic waste from cutting fluids before immobilization in solid matrix
P25	Jordan Bassetti, Christel Pierlot, Arnaud Poulesquen	Understanding the nuclear waste management of organic compounds from cutting fluids with a chemical and formulation perspective
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P30	Caterina Bordin, Bayan Almasri, Youssef Bakkour, Fabrice Bray, Christian Rolando	Identification and unravelling of industrial and artists' alkyd paints and their reticulation using chemical depolymerization and ultra-high resolution mass spectrometry
P31	Frédéryck Tidas, Ritu Toor, Amina Bedaidia, Jean-François Stumbe	Synthesis of a hyperbranched polyglycerol terminated with itaconate groups as novel crosslinking agent for hydrogels
P32	Jean-François Dechézelles, Yaoyao Feng, Fadi Fadil, Véronique Nardello-Rataj	Temperature-responsive Pickering Emulsions Stabilized by Poly(Ethylene Glycol)-Functionalized Silica Particles
P33	Yaoyao Feng, Jean-François Dechezelles, Quentin D'Acremont, Emmanuel Courtade, Vincent De Waele, Marc Pera-Titus, Véronique Nardello-Rataj	Light-driven Pickering interfacial catalysis for the oxidation of alkenes at near-room temperature
P34	Tayeb Ouali, Jean-François Dechezelles, Véronique Nardello-Rataj	Emulsions stabilized by polydopamine particles

Design and physicochemical characterization of poly(butylene oxide)-stat-poly(glycidol) nanoparticles with controlled morphologies and hydrophilic/hydrophobic ratios

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During the last decade, nanoparticulate systems have had a powerful impact on biomedical applications. Various classes of spherical nanoparticles have been designed, mainly by tuning variable parameters of their synthetic identity (e.g., composition, size, surface properties). More recently, a new criterion to control biological processes has been added by conceiving nanoparticles with specific shapes. Understanding how nanoparticles' synthetic identity impacts their interactions with biological systems requires robust technological tools to design particles with controlled properties in a reproducible manner. Not only by handling the shape but also 3D dimensions and surface hydrophobicity because those parameters are interconnected. In this context, we developed nanoparticulate systems with controlled morphologies: sphere, ellipsoidal or hexagonal. The morphology-controlled nanoparticles were composed of statistical poly(butylene oxide)/polyglycidol copolymers (PBO-stat-PG). The copolymers with controlled molar masses and hydrophilic/hydrophobic ratios were synthesized by anionic ring-opening polymerization. Depending on the solubility of the PBO-stat-PG, spherical particles were obtained by emulsion polymerization or nanoprecipitation. Oblate NMs with controlled aspect ratio and curvature radius were designed by the physical deformation of parent spherical particles. Nanoparticles with a typical hexagonal shape and sharp edges were formed by hierarchical supramolecular self-assembly of hydrophobically modified polymers and α-cyclodextrin. Once prepared, the nanoparticles were characterized by electron microscopy techniques (TEM and SEM) and by measuring the zeta potential. Future investigations aim to characterize the impact of nanoparticle morphology and hydrophilicity on their behaviors in biological fluids and after administration in living animals.

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Chitosan-based particles as drug delivery carriers

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Colloidal particles were prepared by physical gelation of an aqueous solution of chitosan mixed with tripolyphosphate (TPP) solution1. These particles were further stabilized by coating with an external layer of alginate. The followed preparation procedure was carried out using only aqueous media and avoided the use of any organic solvent. Particle size distribution was characterized at each step of the preparation procedure using dynamic light scattering and laser granulometry.

Such chitosan-based particles were used for assessing their capacity of encapsulating antioxidant molecules of polyphenol type: catechin, naringin and naringenin. According to the nature of the molecule, very different efficiencies of encapsulation were observed. It was demonstrated that the encapsulation of naringenin was the most efficient among the studied polyphenols.

The kinetics of release was monitored using UV spectroscopy. It was demonstrated that the release of naringenin was limited by the very low solubility of the molecule.

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Oxyacetic derivatives of cashew shell liquid (CNSL) as new bio-based binder for paint preparation

Miarintsoa Michaele Ranarijaona[1], Jean Marie Aubry[4], Sandratriniaina Hermann Rafanoela[1], Fenia Diane Ramiharimanana[1], Lydia Clarisse Herinirina[1], Marie Christine Duclos[2], Alban Léon Lavaud[2], Catherine Goux-Henry[2], Estelle Métay[1,2], Voahangy Vestalys Ramanandraibe[1], Marc Lemaire[1,2]*

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The global coatings industry produces tens of millions of metric tons of paints each year and continues to grow. Most of them are obtained totally or partially from fossil resources and many of them still use VOCs (Volatile Organic Compounds) and other chemicals with high ecological impact.

We describe in this communication the cashew nut shell liquid as a raw material, for paint binder synthesis. These binders are obtained without tedious separation and in a single chemical step form stable films in a short drying time thanks to the association of two mechanisms: the oxidative coupling of the alkylidene chain and the addition of carboxylic acid to the CC double bonds. Paints formulated with this new binder are 100% aqueous require neither drying agents nor VOCs and have low toxicity and ecotoxicity. Moreover, these paints could be applied on different media such as glass slide, metal, wood and concrete. Finally, they exhibit good stability against various solvents and tropical conditions. (fig 1).

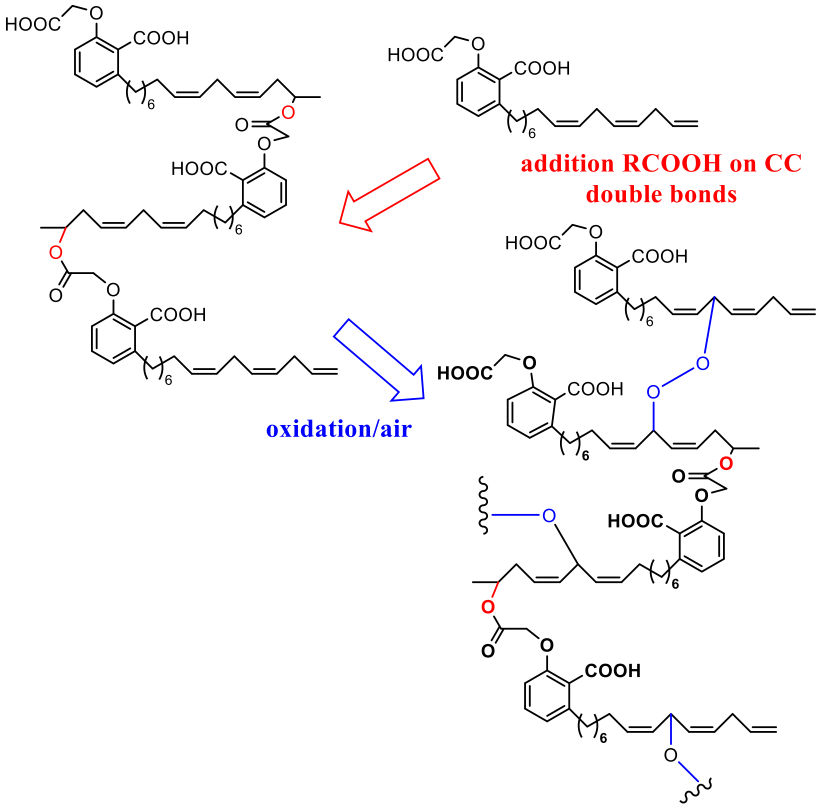

Fig 1. Bio-based paint binder derived from cashew shell liquid (CNSL)

Synthesis and evaluation of amphiphilic molecules from cashew shell liquid (CNSL)

Jean Marie Aubry[4], R. Ny Aina Miangaly[1] , Miarintsoa Michaele Ranarijaona[1], Lydia Clarisse Herinirina[1], Benoit Briou[3], Pauline Fajardie[3], Estelle Métay[1,2], Voahangy Vestalys Ramanandraibe[1], Marc Lemaire[1,2*]

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Cashew Nut shell liquid is obtained by solvent extraction or roasting of the waste of cashew husking of the cashew kernel. In case of solvent extraction 35% of a brown liquid is obtained which contained a mixture of anacardic acid, cardol and cardanol as main products. Moreover this three compounds may contain one two or three CC double bonds. We have synthetized oxyacetic derivatives in one step using sodium chloroacetate and potassium hydroxide. (fig 1)

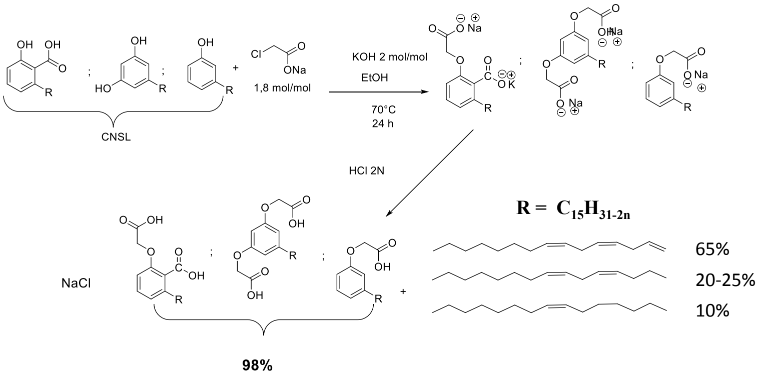

Fig 1. Synthesis of oxyacetic acid derivatives of CNSL

The yield of oxyacetic derivatives of CNSL is very high and the carboxylic acid mixture can be easily transformed into sodium salt which is completely soluble in water and forms a stable foam like sodium dodecyl sulfate (SDS) and sodium salt of linear alkyl benzene sulfonic acid. (LABSA).

This mixture of amphiphilic molecules has surfactant properties similar to those of petro-based industrial surfactants such as SDS and LABSA but with a much smaller CMC. In addition, the toxicity towards normal human dermal fibroplasts (NHDF) and normal human epidermal keratocytes (NHEK) is much lower than that of the two industrial surfactants mentioned above. Finally, the aquatic toxicity was also evaluated on the nauplii of Atermia catvis and also proved to be much lower compared to SDS and LABSA.

Given the potential availability of CNSL, a by-product of the cashew nut industry which is marketed at more than 2 million metric tons/year, this new surfactant may be of great technical and economic interest.

References:

Development of Sustainable Chemistry in Madagascar: Example of the Valuation of CNSL and the Use of Chromonesas an Attractant for Mosquitoes
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Molecules **2021**, 26, 7625

NextBioForm: Centre for formulation and development of next generation biologics

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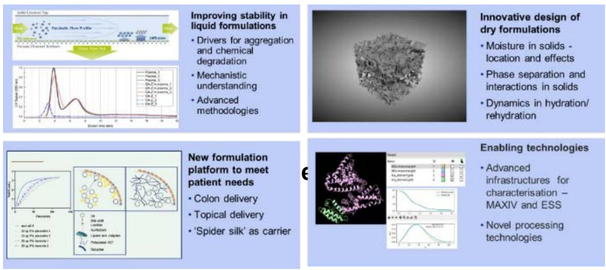
NextBioForm is a one-of-a-kind competence center providing cutting edge research on industrially relevant issues for formulation and characterization of biologically based drug products. We aim to deliver new and improved formulations which will bring stable biopharmaceuticals to the patients and thus support improved quality of life. The center gathers 20 partners from the institute, academic, hospital and industry sectors and are funded by the Swedish Agency for Innovation Systems, Vinnova, and the Swedish Research Council through their biologics program. The broad range of expertise within the center provides a unique opportunity to verify methodology and techniques on both well-known and new biologics.

The research within NextBioForm is focused on formulations and processing of biologics, specifically proteins and probiotic bacteria, and is divided in four work packages. The aim of work package 1 is to improve stability of liquid formulations by creating rational approaches and fundamental understanding of how proteins in solution are physically and chemically affected under different conditions. We develop and combine advanced characterization methods, such as flow field fraction, miniTEM, SAXS and SANS with more classical techniques to generate new insights in the mechanisms behind protein stability in formulations [1]. Work package 2 is focused on innovative dry formulations and drying technologies to improve stability of biologics and allow for long-term storage also at room temperature [2]. The focus of the research is the intimate interplay between water, biologic and the excipients in a solid-state formulation using e.g., calorimetry and SAXS [3]. These different factors contribute to the stability of the active ingredient and are thus important to investigate and understand. The aim of the third work package is to develop novel formulation concepts for biologics that can provide stability, targeted delivery, and improved functionality for the patient. The focus is on concepts that can provide local delivery to the skin and the GI tract [4]. Local and targeted delivery is important to reduce side effects of drugs. Moving from injections to oral or topical therapy would be a huge improvement with respect to quality of life for the patient. The fourth work package focuses on new characterization methods for biologics and drug formulations by using large research infrastructure, such as the MAXIV synchrotron, to understand the complex science that governs stability in biologics. Specifically, we develop and commission new sample environments suitable for investigating formulations of biologics. The different work packages work closely together to advance the science for understanding the stability of biologics in formulation and delivery.



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RealHOPE – Real World Handling of Protein Drugs: Exploration, Evaluation and Education

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Many new medicines are based on proteins, which have improved the lives of people with a range of diseases. The development, production, distribution, and handling of these drugs still present challenges that need to be addressed to generate further evidence on stability, and therefore safety and efficacy during handling in use.

The RealHOPE project focuses on creating an understanding of the real-life handling of protein drugs in hospital/community pharmacies, clinics, transportation and in the hands of patients. Our research covers in-use aspects of protein pharmaceuticals, investigating the critical steps where stability can be compromised. With the goal to support a safe and efficient use, we will develop tools for simulation of real-life events, mitigation of critical handling steps, and tailored education to ensure careful handling by healthcare and pharmacy staff as well as patients and caregivers. The project will include measurements of real-life handling during transportation and by healthcare personnel and patients using smart tag technologies. The data will be used to develop new methods to simulate reallife events. The project also includes interviews with stakeholders to create a better picture on how protein drugs are handled today and how to educate stakeholders in the future.

RealHOPE is an IHI-funded project that brings together 24 partners across EU, UK, Switzerland, and USA, representing major pharma companies, academia, hospital pharmacies and clinics, patient organizations as well as SMEs in logistics, analytical tools, and apps for education and disease monitoring. This presentation will introduce the project and the multidisciplinary approach to improve the use of protein drug products.

Synergistic Effect of Flowback Aid Surfactants for Maximum Efficiency: Understanding Physicochemical Properties and Fluid Recovery

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The exploration of hydrocarbons from unconventional reservoirs has increased considerably in recent years (as noted in Figure 1) due to developments in the hydraulic fracturing method, which consists of the extraction of oil and gas from a reservoir of difficult access (mainly shale) through the construction of a horizontal well and then injection of fluid under high pressure, causing the formation of fractures [1]. From forming such fractures, channels with greater permeability are created, allowing better extraction of oil/gas from the reservoir [2].

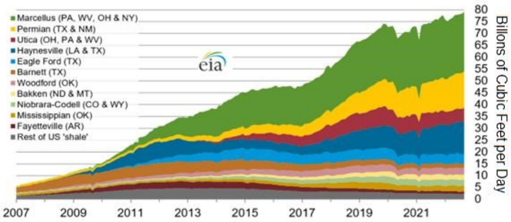

Fig 1. Evolution of shale gas production in the US since 2007 (EIA: Energy Information Administration - EIA - Official Energy Statistics from the U.S).

However, a large part of the aqueous fracturing fluid injected remains trapped in the reservoir due to the capillary pressure effect causing a decrease in well productivity, especially in low permeability formations [2]. Therefore, surfactants are often added to fracturing fluids acting as flowback aids, which are mainly concentrated on the surface of the fracturing fluids and at its interface with the reservoir hydrocarbons. The purpose of using flowback aids in fracturing fluids is to improve the recovery of the injected fluids and, consequently, the oil and gas production [3]. In this study, a series of flowback aid surfactants (nonionics) were evaluated, aiming to obtain optimized formulations that address the target properties, such as low critical micellar concentration (CMC), low surface tension (ST), high cloud point (CP) and high capillary contact angle (CCA), as well as to improve fluid recovery and prevent emulsion formation through the combination of surfactants and solvents. A flowback aid with a low CMC is interesting, as it shows that the flowback aid can be used in low dosage. The low surface tension of a fracturing fluid is related to its greater malleability and, consequently, its ability to deform and pass through narrow channels into the formation [4]. The high cloud point is related to the greater stability of the solution at high temperatures [5]. The effect of capillary pressure, which can be related to the measurement of the capillary contact angle, is extremely important to correlate the recovery of injected fluid and, consequently, the impact on well productivity and the reduction of damage caused to the formation [6]. And the prevention of the formation of emulsions makes the separation between the injected water that returns to the surface and the produced oil happen quickly [5].

It was possible to observe the relevant effect of the degree of ethoxylation for the adjustment of the properties of interest since the increase in the degree of ethoxylation improved by raising the cloud point but worsened by increasing surface tension and critical micellar concentration. Three surfactants were pre-selected and divided into two classes of wetting agents (tallow amine 8 EO) and surface tension reducers (lauryl alcohol 7 EO and isotridecyl alcohol 9 EO) and evaluated with the solvent isopropanol as it shows the best effect of increasing the capillary contact angle. Therefore, a Design of Experiments (DoE) was proposed to investigate the synergistic effect of those pre-selected surfactants.

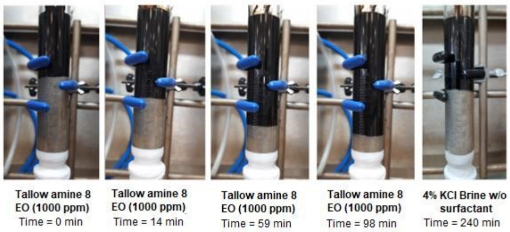
Tallow amine 8 EO (1000 ppm) Time = 0 min
Tallow amine 8 EO (1000 ppm) Time = 14 min
Tallow amine 8 EO (1000 ppm) Time = 59 min
Tallow amine 8 EO (1000 ppm) Time = 98 min
4% KCl Brine w/o surfactant Time = 240 min

Fig 2. Fluid recovery test using an offshore crude oil (API 21°) with 1000 ppm of tallow amine 8 EO in the brine of 4% KCl over time and blank (brine of 4% KCl without the addition of surfactant).

During the design of experiments (DoE), two optimized formulations were identified, and after the advanced tests of crude recovery (exemplified in Figure 3) and emulsion prevention against single surfactants, it was possible to observe a synergic effect of the optimized formulation containing isopropanol, tallow amine 8 EO and lauric alcohol 7 EO presenting the best fluid recovery time and a high emulsion prevention effect.

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NucleoDry – Research project for enhancing stability of gene therapies

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Vaccine formulations with demanding storage conditions became a challenge for the world during the pandemic. Transportation and storage have required an advanced cold supply chain only available in the richest countries. Methods for producing vaccines stable at 4°C would decrease the demands on transportation and storage, make the distribution cheaper and more available world-wide. NucleoDry aims to develop production processes for manufacturing of mRNA medicines that remain stable at 4 °C instead of −80 °C. The processes are based on lyophilization which is a gentle technique for enhancing stability of biological modalities under milder conditions. However, understanding how removing water affects the particle nanostructure after rehydration remains challenging. NucleoDry has a goal to build up new infrastructure for vaccine development to contribute creating generic solutions for development of stable mRNA vaccines and pharmaceuticals. The project is being run by RISE together with Karolinska Institutet, Vecura at Karolinska University Hospital, and the Swedish innovation and manufacturing company NorthX Biologics. NucleoDry brings together expertise spanning the entire care chain from mRNA production via formulation development to scaling of manufacturing processes for large-scale pharmaceutical production.

Gels of Plant-based Protein Concentrates

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Current trends in the food industry follow the ongoing shift towards more sustainable solutions. One area in need of a larger focus is the development of plant-based analogues to dairy products. The major challenge for the industry is to develop products that constitute the same properties as animal derived products, both regarding the nutritional value, as well as texture and taste. Pulse crops, such as peas and faba beans, are attractive starting materials due to their higher protein content compared to other legumes. The functionality of the proteins is determined by their physio-chemical properties, such as gelling and emulsifying properties, and can be influenced by adjusting pH or addition of salt, such as different phosphate salts.

This project has investigated the properties of faba bean protein concentrates produced in Sweden. Physio-chemical properties of such as denaturation temperature and zeta potential were investigated, as well as the solubility and its dependency of pH and salts have been investigated. Emulsification of rapeseed oil and coconut oil at neutral pH and at 5.5. Lastly gelling was investigated as a function of pH and addition of different salts.

Typically, 10-20% of pulse proteins are water soluble albumins, and 70-80 % of pulse proteins constitutes of globular proteins that are salt soluble. The soluble fraction at natural pH (6.7) with no added salt was approximately 18 w/w% of the total protein content for faba bean concentrate. This is in line with what could be expected for the albumin content in pulse concentrates.

It is well known that the solubility of proteins is affected by pH, and is the lowest around the proteins isoelectric point, while it increases with higher or lower pH. However, the effect is much larger for globulins than albumins as shown by a study of kidney bean proteins [1]. For the faba concentrate the iso electric point was at pH 4.5.

Our results show that some types of salts affect the protein solubility (see Figure 1) and the gelling properties of the faba protein concentrate. These effects will be discussed in more detail.

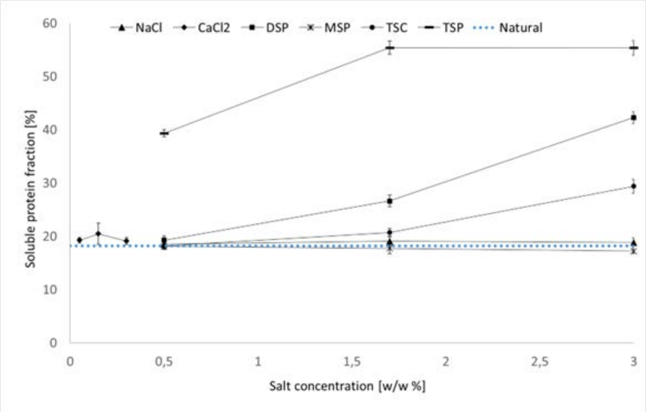

Fig 1. Soluble fraction of faba bean protein concentrate in the presence of different salts. DSP=Disodium phosphate, MSP= monosodium phosphate, TSC= Trisodium citrate, TSP= Trisodium phosphate, Natural pH =pH 6.7 for faba bean.

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Microencapsulation and surface priming of fine porous particles

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Encapsulation technology has been used in industries such as food, pharma, and agrochemical for many years1 with the purpose to protect the active ingredients and release them in a desired manner when needed. For an increased product efficiency, the encapsulated active ingredients have to be protected not only from the external environment but also from the internal supporting structure (pore surface) as issues with chemical degradation might occur. Additional difficulties come with the size, the smaller the particles the more difficult it is to control the coating process, and for particles below 50 microns it is almost impossible do that with common technologies such as fluid bed coating2. This sets a clear restriction for product developments for food, pharma, and agrochemical industries. These challenges could essentially be addressed by using the supercritical (sc) CO2 medium: surface priming in a first step followed by particle coating in a second step.

As model host particles, or carriers, we have used porose silica particles, brand name Syloid (about 3 microns in size), and porose Kromasil particles (7 microns in size) to demonstrate the ability of surface priming. For demonstrating the ability for overall coating, we have used dense cellulosic particles - brand name Cellets (about 350 microns in size). For both surface priming and overall coating, we have used the following polymers: hydroxy propyl cellulose (HPC), ethyl cellulose (EC) and Eudragit (L100 and L100-55). The change in the pore volume and surface area before and after polymer treatment was measured using BET and for imaging SEM was used.

Syloid particles were treated with 4wt% of each of the following polymers: Eudragit, HPC and EC. Kromasil particles were treated with only Eudragit polymers at 4wt%, 20wt% and 33wt%. Here only representative results are presented. As expected, the SEM images of Syloid particles (not shown here) before and after polymer treatment do not differ at all because the polymer precipitated inside the pores, likely on the pore walls. This result was confirmed by the BET measurements, presented in Table 1, which clearly show drop in surface area when treated with 4wt% polymer as compared to reference. The same trend was observed for Kromasil. The data shows that with increasing the total content of Eudragit polymer both the external surface area and the specific surface area (BET) are shrinking as compared to untreated material (reference) demonstrating the increased thickness of the deposited polymer layer. Here, however, due to the regular shape of the particles, one could observe the presence of the polymer at high polymer concentrations. For the overall surface coating experiments,Cellets particles were treated with HPC, Eudragit, and EC polymers at varying coating weights (from 2-50wt%). Sem images showed a coating with 4wt% HPC with the ability cover the particle with a tiny polymer layer. Additionally, from 2-33wt% a good flowability of the particles after polymer treatment was obtained. However, this parameter seems to be dependent on the CO2 exposure time, the ratio between solvent and antisolvent (CO2), and ability to extract the solvent of the polymer.

In this work we have demonstrated that scCO2 has the ability to both surfaces priming fine porose particles and lay an overall coating on dense particles. First, by surface modifying the interior of porose particle, that is depositing a polymer layer on the pore walls, one could eventually protect sensitive ingredients that are loaded in this media from the active species present on the internal pore wall. Second, by laying an overall coating on particles loaded with active ingredients one could protect the active ingredients from external stimuli as well as control their release. Our vision is to scale up these results into industrial processes that could stimulate growth in the food, pharma, and agrochemical industries.

Table 1.

Syloid system	Reference	4wt% L100-55	4wt% EC N10
Ext. surface area [m²/g]	342	280	295
SSA (BET) [m²/g]	351	313	321

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Evaluation of the adsorption properties of fibroin peptides

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Silk is a biopolymer produced by different varieties of silkworms. Mulberry silk is obtained from the silkworm *Bombyx mori L*., which feeds exclusively on the leaves of mulberry plant[1]. Silk is thought to be the oldest and valuable textile material due to his good mechanical properties. It is composed of two kinds of proteins: fibroin, a fibrous protein, that imparts mechanical strength to the cocoon, and sericin, a glue-like protein, that binds the fibroin fibers together in a cocoon.[2] The silk fiber for textile is produced by removing sericin protein to give the softness and the lustrous appearance to the silk fiber. In addition to its use in textile industry, fibroin fibers are used in biomedical applications due to their biodegradability, biocompatibility and low immunogenicity. The appropriate mechanical properties of silk fibroin as biomaterial are major perquisite for its use in bioengineering. Moreover, various drugs can be loaded or encapsulated using silk fibroin as nanoparticle.[2,3]

In order to diversify and improve the functional properties of fibroin, the hydrolysates obtained by acid or enzymic hydrolysis can be considered for applications in foods, cosmetics and pharmaceutical preparations. Fibroin hydrolysates also have been suggested as an antidiabetic, antioxidant and antihypertensive agent.[4,5] Silk protein derived peptides represent a great potential in cosmetic industry as cosmetic additives (antioxidant, cleaning, moisturizing and restoring agent). Silk fibroin is composed of different amino-acids with hydrophilic and hydrophobic domains which imparts potential amphiphilic properties to this protein. This class of amphiphilic molecules is interesting since it derives from non-food raw material so it doesn't give rise to ethical and environmental concerns as compared to surfactants produced from food biomass (sugar, starch, vegetable proteins). Nevertheless, the evaluation of surface adsorption properties of silk fibroin peptides remains little described.

The main objective of this work is to evaluate the potential of fibroin peptides to reduce surface tension for the production of silk-derived amphiphilic molecules. The first step involves the separation of two fractions of silks derived from silkworms: sericin and fibroin, using standard procedures largely described in the literature.[6,7] After extraction, silk fibroin solution is directly hydrolyzed using Alcalase enzyme under different experimental conditions, varying the amount of enzyme and the reaction time. The degree of hydrolysis (DH), is determined by the absorbance measurement of primary amino groups by o-phtaldialdehyde (OPA) method. Finally, the adsorption properties of the hydrolysates were evaluated by surface tension measurements using the pendant drop method.

The results demonstrated that DH of fibroin is mainly affected by the enzyme/substrate ratio, but not significantly influenced by the reaction time. The first results on the surface tension measurements showed the good ability of fibroin peptides to reduce the air/water surface tension (Fig 1). This underlines the interest of their potential of use as amphiphilic molecules. Future research will be focused on the functionalizing of fibroin peptides by grafting of hydrophobic chains for improving of their amphiphilic character.

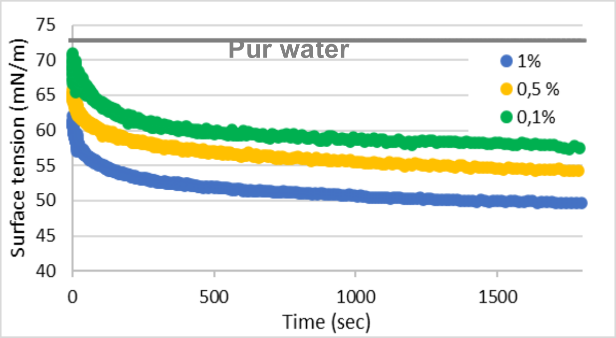

Fig 1. The surface tension of fibroin peptides at different concentrations

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P 12

Saponins from *Furcraea foetida*, a comparative study on amphiphilicity, emulsifying and foaming properties

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A sustainable surfactant was obtained as a by-product of waste from the production of fibers from *Furcraea foetida* (FF) in the hemp of Mauritius in Madagascar. The hypothesis of surface-active behavior of this crude mixture was corroborated by surface tension measurements and these results were compared with 2 commercial Quillaja saponaria (QS) samples: S0019 (TCI) and Q-Naturale 200 V. The hydrophilicity-lipophilicity radius was determined by the PIT-slope method and all saponins are more hydrophilic than the $C_{10}E_4$, the polyethoxylated reference surfactant. The hydrophilicity decreasing order is as follows: Q-Naturale 200 V > FF> S0019. Oil in water (O/W) emulsions were formulated with isopropyl myristate as oil and their size distribution and stability during 7 days are equivalents for the three saponins. There is no coalescence, and creaming phenomena can be reduced increasing the oil fraction. Nanoemulsions were obtained with FF using ultrasounds and reducing the oil content. Foaming properties were also studied and the stability of foams is similar between the 3 saponins (higher than the foam formulated with sodium laureth sulfate). These findings show that FF is a new source of saponins that can be used as promising emulsifier and foam agent with properties equivalent to those quantified for available commercial saponins and equal or better than typical benchmark surfactants as Tween 40 (emulsifier) or sodium laureth sulfate (foaming agent).

Fig 1. Extraction of Saponins from *Furcraea foetida*

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Influence of formulation, composition and process variables on the properties of organogel-based water-in-oil emulsions

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Organogel is a three-dimensional supramolecular network formed with an organic solvent and a gelling agent by chemical or physical interactions. They have several applications in drug delivery, food and in the formulation of cosmetics, supercapacitors and as pollutant molecules trap. For example, in food they have emerged as a promising alternative for producing semi-solid fats with reduced saturated fatty acid content [1-2]. These gelled oils can also be used to stabilize water-in-oil emulsions, thus further reducing the fat content in culinary preparations. The use of organogels to stabilize emulsions is indeed a way to confine the dispersed phase droplets and drastically limit coalescence. The influence of some preparation variables (*i.e.* cooling and shear rates) on the final physico-chemical properties of organogels have been reported [3] but there is a lack of their influence on the W/O emulsion formulation.

The present work aims at exploring the role of low molecular weight organogelators such as glycerol monolaurate (GML) and 12-hydroxystearic acid (12-HSA) in the gelling of vegetable oils (sunflower seed oil – SSO) and organic solvents, and presents a use of these gelled oils to form reverse emulsions. Gels have been investigated as a function of their structural differences and linked to Hansen solubility parameters that can predict the gel formation [4]. To assess the influence of the type of gelator, mechanical and thermal properties of 3 wt% 12-HSA/SSO and GML/SSO organogels have been analyzed. Glycerol heads of GML aggregate as the hydrophobic chains are brought together through Van der Waals interactions whereas the polar heads of 12-HSA are able to form spherulitic-like aggregates in vegetable oils and form a stronger network than GML. In addition, organogelled W/O emulsions have been made with both organogels. Analysis have proved that the heterogeneity in size water droplets for this type of emulsion are sterically stabilized by the three-dimensional network preventing coalescence. The shape and size of the droplets seem to be modified by the mixing technique used and the cooling rate of the organogel emulsions. Finally, a water volume fraction gradient has been performed to highlight the stability limit of 3 wt% 12 HSA/SSO organogel emulsions. At a water mass fraction of 45 %, a two-phase mixture has been obtained comprising a W/O emulsion and an aqueous excess phase.

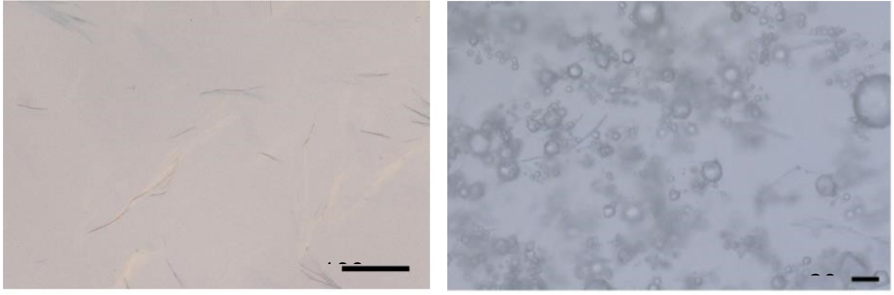

Fig 1. Micrographs of 3 wt% GML/SSO organogel (left) and an emulsion an emulsion whose dispersed phase is 10% water in the same gel (right)

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Self-aggregation, dilational surface rheology and foaming properties of 1-O-dodecyl diglyceryl ether compared to other non-ionic surfactants

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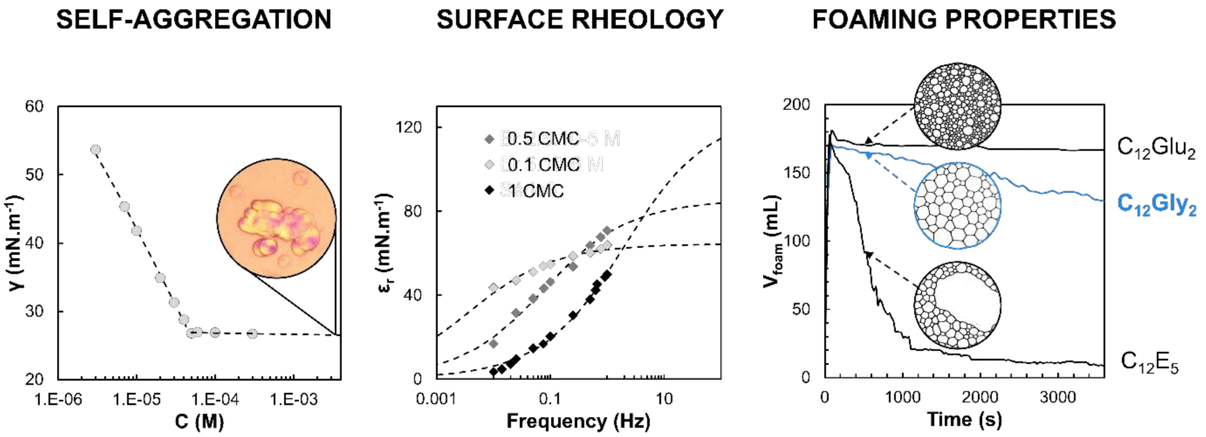
Diglyceryl alkyl esters are good foaming agents but the ester linker can be sensitive to pH, chemicals and temperature unlike the ether function. In this work, the foaming properties of a diglyceryl ether, namely 1-*O*-dodecyl diglyceryl ether ($C_{12}Gly_2$), are compared to those of *n*-dodecyl-β-D-maltoside ($C_{12}Glu_2$) and pentaethyleneglycol monododecyl ether ($C_{12}E_5$). The self-aggregation behaviour of $C_{12}Gly_2$ and adsorption at the air-water interface has been first investigated. For the three surfactants, the dynamic response of the interface, measured in oscillatory bubble interfacial rheology experiments below CMC, is compared and put in relation with their foaming properties. In particular, the foamability by air sparging at a concentration of 10 times the CMC, the foam stability over 1h and the foam density are quantified.

It is shown that $C_{12}Gly_2$ forms liquid crystals at low concentration (~10 CMC). $C_{12}E_5$, with a lower elasticity high frequency limit ε_0, forms unstable foam with quick drainage and breakdown, whereas higher ε_0 surfactants $C_{12}Gly_2$ and $C_{12}Glu_2$ form much more stable foams, resulting from hydrogen bonds between the polar heads of $C_{12}Glu_2$ and $C_{12}Gly_2$. Differences in $C_{12}Gly_2$ and $C_{12}Glu_2$ foams lay in initial bubble size (smaller for the $C_{12}Glu_2$). In $C_{12}Gly_2$ foam, the main destabilization phenomenon is coalescence over drainage, and the foam volume only decreases by 30% in 1 hour.


SELF-AGGREGATION

SURFACE RHEOLOGY

FOAMING PROPERTIES

Fig 1. Surface Tension profile, dilational rheology and Foam Volume profile of 1-O-dodecyl diglyceryl ether.

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Rational design of W/O nanoemulsions using the normalized HLD concept and the formulation-composition map

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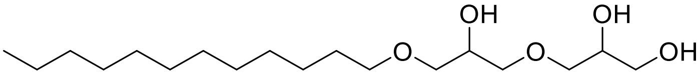
The 1-*O*-dodecyl diglycerol ether ($C_{12}Gly_2$) is a novel and well-balanced bio-based surfactant.



Its amphiphilic behaviour is rationalized within the Normalized Hydrophilic-Lipophilic-Deviation (HLD_N) framework (Eq. 1), allowing to design $C_{12}Gly_2$/Oil/Water micro- macro- or nano- emulsions with desired features (type, viscosity, stability, water/oil ratio).[1,2]

$$HLD_N = PACN - EACN + t.(T - 25) + d.S \qquad (1)$$

Where PACN expresses the hydrophilic/lipophilic ratio of the surfactant at 25°C, EACN is the oil hydrophobicity, T the temperature (°C), S the salinity (wt.% NaCl) whereas t and d reflect the surfactant sensitivity towards temperature and salinity respectively.

Its actual amphiphilicity in saline and salt-free media was measured by two methods. The first, classic but tedious, is based on the identification of the optimal formulation in a series of tubes containing $C_{12}Gly_2$/n-Alkane/Water (SOW) systems at equilibrium. The alternative method, much faster and more precise, is based on the phase inversion of the same systems under stirring, the HLD value of which is gradually modified by changing the temperature or the salinity.[3,4]

The systematic variation of the W/O ratio and of the temperature makes it possible to construct a Formulation/Composition map. This map is a powerful tool to predict which type of emulsion (O/W, W/O or multiple) will be obtained depending on the composition of the SOW system and the emulsification protocol used. In particular, it is possible to prepare stable and very fine emulsions (≈ 100 nm) by crossing one of the areas of the map favouring the splitting of the droplets and then moving away from it quickly to prevent the coalescence of the droplets

Keywords: Normalized Hydrophilic-Lipophilic-Deviation, Phase Inversion, Nanoemulsions

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TiO$_2$ nanoparticle dispersions studied by sedimentation analysis: Hansen Parameters vs. DLVO interpretations

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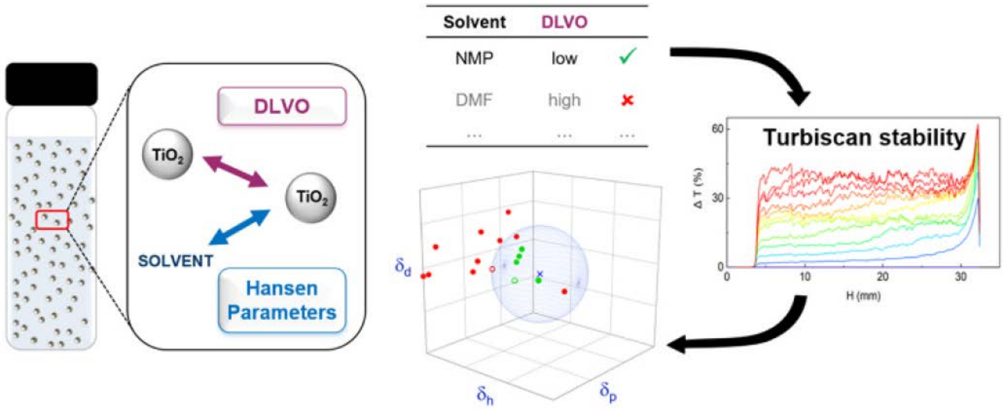
Hansen Solubility Parameters (HSP) have been shown to be an effective approach for rationalizing and predicting the stability of titanium dioxide nanoparticles (TiO2 NPs) dispersions. However, interparticle electrostatic interactions, not considered in Hansen's approach but taken into account in the DLVO theory, are expected to play a significant role in organic solvents having a notable dielectric constant. Zeta potential ζ of TiO2 P25 NPs was measured in both aqueous and organic media to identify DLVO-stabilized dispersions from those stabilized by more specific NP-solvent interaction. Stability was quantified using a Turbiscan optical device which provides Stokes diameters and Relative Turbiscan Stability Index (RTSI). When the zeta potential of NPs and the dielectric constant of the solvent are both high, the dispersion benefits from additional stabilization while when the electrostatic repulsion is negligible, only the solvents within a Hansen dispersion sphere give stable dispersions. The two interpretations are therefore complementary to describe the behavior of TiO2 dispersions in organic solvents.



Solvent	DLVO	
NMP	low	✓
DMF	high	✗
...	...	...

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Innovation in biobased surfactants from carbohydrate-based furanic platform molecules

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Biomass is tomorrow's resource for chemistry [1]. Carbohydrate-based furanic platform molecules offer original scaffolds for the design of novel chemical architectures [2]. Using the Morita-Baylis-Hillman (MBH) reaction, a series of new furanic amphiphiles has been prepared from the coupling of HMF, GMF or SMF (succinate derivative of HMF) as biobased furanic aldehydes with hydrophobic activated alkenes [3]. Structural variations include the level of polarity on the furanic substrate (HMF, GMF and SMF), the type of activated alkenes (ester or amide) and the alkyl chain length and level of saturation. The physicochemical properties of these original systems were evaluated. Some of them exhibit interesting abilities to lower the water surface tension. Using the PIT-slope method [4], the newly synthesized compounds were compared to other types of surfactants, including previous series of carbohydrate-based amphiphiles

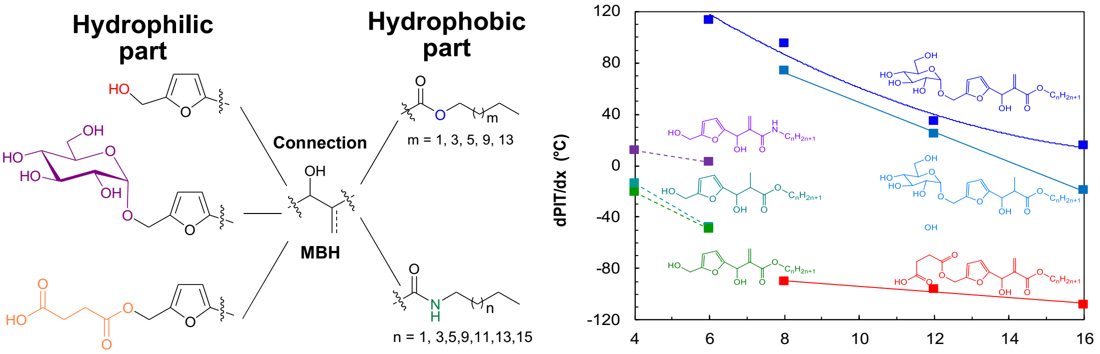

Fig. 1: Structural variations in novel MBH adducts from HMF, GMF and SMF, and comparison of their amphiphilicity through the PIT slope method

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Characterization and analysis of some macromolecular compounds coated with essential oils

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Essential oils obtained from plants are complex mixtures of volatile compounds. Since ancient times, essential oils (EO) have been widely used in folk medicine, food flavoring and preservation, and perfumery. All of these oils have recently gained popularity and scientific interest. According to recent studies, insects, parasites, bacteria and fungi are all susceptible to the biocidal effects of essential oils (EOs) [1].

But these oils are chemically unstable and susceptible to oxidative deterioration and loss of volatile compounds, especially when exposed to oxygen, light, moisture and heat.

In this context, we are interested in the physico-chemical behavior of some essential oils with soft matter (complex polymeric systems, gels and thin films).

In this work, we propose a sodium alginate-based biofilm (alginate is the most biocompatible wall material used in cell encapsulation technology)coated with essential oil (Rosemary-Myrtus) with in some cases the addition of PEG (polyethylene glycol).

Rosemary (Rosmarinus) -Myrtle are a very abundant species in Tunisia, used in popular medicine, cosmetics and phytopharmacy. The extraction of essential oils was carried out by steam distillation..

Several studies have noted the need to evaluate the thermal, mechanical (tension, flexibility), optical, wettability and morphological properties of the films [2,3,4].

These biofilms have been characterized by the water contact angle technique and by dielectric measurements using an impedance analyzer.

These synthetic membranes exhibit hydrophilic or hydrophobic behavior, the surface energy of these films depends on the composition of essential oils [5]. The elasticity, morphology and porosity of these films are studied.

UV-Visible spectroscopic analyses on our biofilm are in progress: transmittance (T), reflectance (R), absorbance (A) and absorption coefficient; the value of the extinction coefficient (k), the refractive index (n), the real and imaginary parts of the dielectric constant of the film spectra have been determined. Tauc diagrams of our films were used to determine the gap energy (3.6Mev) [6-7].

Food and nutrition remains a very important topic of interest. The activity of essential oils on pathogenic bacteria shows that the antimicrobial power of these oils is very important. The use of essential oils can be an effective alternative to fight against foodborne infections in the face of increasing antibiotic resistance .

A particular interest in our studies is the field of encapsulation which has progressed enormously with the introduction of encapsulated products of micro and nano size in the form of powders, emulsions, beads, films [8].

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Formulation of chemically curable Silicone for kidney surgery training

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Due to the improvement of surgery techniques for kidney cancer, surgeons are in need of new materials and techniques for their training. The project consists in the development of a 3D printing technique of patient-specific kidney and tumour phantoms made of specifically formulated silicone. [1]

My work focuses on the 3D printed silicone mix formulation. Three routes of functionalization are considered in the attempt to match the final material with living kidney characteristics:

- Modification and control of the final material mechanical properties
- Establishment of a pseudo-vascularization in the material
- Creation of a fluid release mechanism at the cut of the material

In order to achieve these, we consider the silicone formulation with the inclusion of water drops through the emulsification of water inside the polymer fluids before its crosslinking.

Indeed, the addition of water droplets in the material, in some specific conditions, should make it softer. Plus, the connected emulsion formulation should imply the water release at cut and allow us to create the pseudovascularisation. [2]

The control of water content, drop size and emulsion morphology should therefore enable us to functionalize the materials in a controlled way and thus, create a phantom mimicking at best the living kidney.

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Influence of oil properties on Pickering emulsions stabilized by quercetin

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Emulsions are nowadays widely used in food, pharmaceutical and cosmetic applications. These systems are useful to encapsulate an active ingredient in a dispersed phase, to protect it from degradation and to preserve its activity in a sustained manner. However, they are thermodynamically unstable systems and thus, require the use of stabilizers in their formulation for a long-term stability [1]. Surfactants or polymers are commonly used as stabilizers but raise direct or indirect toxicity and environmental issues. For instance, in topical long-term treatment, skin irritation is often observed [2].

To circumvent toxicity risks, solid particles can be used to stabilize emulsions, referred to as Pickering emulsions. In addition, these emulsions have increased stability compared to conventional ones prepared with surfactants, because the particles are irreversibly anchored at the interface and form an effective protection against destabilization phenomena such as coalescence [1].

Targeting pharmaceutical applications, our work focuses on Pickering emulsions stabilized by quercetin particles. Quercetin is a natural flavonoid compound, easily found throughout in fruits and vegetables. It exhibits a variety of pharmacological activities such as anti-inflammatory, antioxidant, anticancer and neuroprotectant [3]. However, if quercetin has attracted much attention of dietitians and medicinal chemists in the recent years, its very low solubility in water limits its oral bioavailability. We imagined benefiting from this drawback by stabilizing Pickering emulsions with quercetin particles. Thus, it makes possible to stabilize the emulsion directly by an Active Pharmaceutical Ingredient (API) or even to encapsulate a second biologically active substance in the emulsion.

The aim of this study is to investigate the influence of oil properties, and especially oil polarity, on the formation and stability of Pickering emulsions stabilized by quercetin particles. Indeed, previous studies have shown that the choice of the oily phase has a great influence on the emulsion formed and its stability [4, 5]. Various types of oils of different polarities are chosen as the oil phase to prepare the Pickering emulsions. The stability of the emulsions is characterized macroscopically, by microscopy and measurement of droplet diameter.

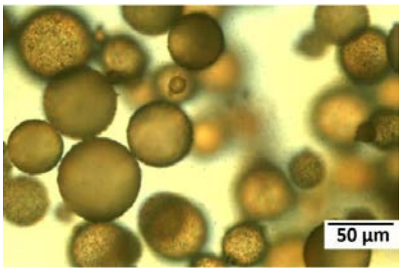

Fig 1. Optical microscopy image of an oil-in-water Pickering emulsion prepared with quercetin and MIGLYOL® 812 N.

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Adsorption of Sulfur-Type Extreme-Pressure Agent

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Lubricants are generally composed of base oils and additives. An extreme pressure (EP) agent is a lubricant additive, which can form a reaction film on a metal surface under sliding conditions at high temperatures and high pressures. The reaction film prevents the metal surface from wearing. In the aspect of industry, it is necessary to study the effect of temperature on the adsorption behavior and the reaction film composition of EP agents on metal surfaces, necessarily influencing their tribological properties. In our previous studies, we proposed that the adsorption of EP agents that occurs at solid/liquid interfaces is an important process in the early stages of sliding[1-2)]. Herein we characterize the adsorption/desorption of a sulfur-type EP agent on/from an iron oxide substrate at different temperatures, and analyze the composition of its reaction film after frictional treatments. The sulfur-type EP agent is an environmental additive, and is used in a variety of industrial applications.

The sulfur-type EP agent used in this study was 10,10'-trisulfanediyldistearic acid, synthesized from fatty acid. *n*Dodecane was selected as a model base oil. Iron oxide (SPCC) was used as a solid substrate. The adsorption/desorption of the sulfur-type EP agent on/from the iron oxide substrate was characterized by means of a quartz crystal microbalance with dissipation monitoring (QCM-D) technique. The measurement temperatures were set at 25, 40, and 55 °C. The coefficient of kinetic friction was measured using a ball-on-plate type friction analyzer.

QCM-D results are shown in Figure 1. The concentration of the EP agent was set at 1 wt%. The injection of the EP agent resulted in decreased frequency at the three measurement temperatures. This result suggests the adsorption of the EP agent to occur on the substrate surface. The frequency shift observed at 55 °C was smaller than those observed at the other temperatures, reflecting the adsorption inhibition at high temperatures. This may arise from the increased solubility of the EP agent in the base oil at high temperatures[1)]. The frequency shift did not return to the original baseline level even when the solution was again replaced by *n*-dodecane; i.e., an adsorption film remained on the substrate surface. In this presentation, we will discuss the effects of temperature and chemical structure of the sulfur-type EP agent on the adsorption and friction behaviors.

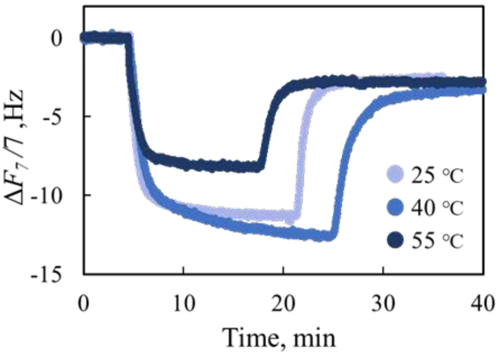

Fig 1. QCM-D frequency changes observed in *n*-dodecane with the sulfur-type EP agent (1 wt%).

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Real-time observation of fatty acid cleaning: QCM-D measurements

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Keeping the body clean by removing sebum stains is important for maintaining good health. The cleaning of fatty acids is a complex phenomenon that depends on various conditions such as temperature and concentration of detergents. Therefore, it is not easy to monitor the cleaning process quantitatively in real-time [1, 2].

In this study, we characterized the cleaning process of fatty acids by means of a quartz crystal microbalance with dissipation monitoring (QCM-D) technique. Sodium dodecyl sulfate (SDS) was used as an anionic surfactant (detergent). Two solid fatty acids, palmitic acid ($C_{16:0}$) and stearic acid ($C_{18:0}$), were employed in this study and spincoated on a QCM-D silica-coated sensor pre-treated by a silane coupling agent.

The typical QCM-D results are shown in Figure 1. In these measurements, the baseline was obtained in air, and then pure water was injected into a QCM-D flow module at different temperatures (25 ºC, 35 ºC and 45 ºC). Significant increases in viscosity and density resulted in decreased frequency ($\Delta F_3/3$) and increased energy dissipation (ΔD_3) at this stage. In the subsequent step, an aqueous solution of SDS (25 mM) was further injected into the module. This solution replacement resulted in increased $\Delta F_3/3$ after detecting a local minimum. This result suggests the adsorption of SDS on the spin-coated $C_{16:0}$ film and the subsequent desorption of the SDS + $C_{16:0}$ complex into the bulk solution phase. This behavior was strongly dependent on the measurement temperatures, reflecting different cleaning mechanisms such as solubilization, emulsification, and rolling-up. We will discuss the cleaning mechanism on the basis of the resultant QCM-D data.

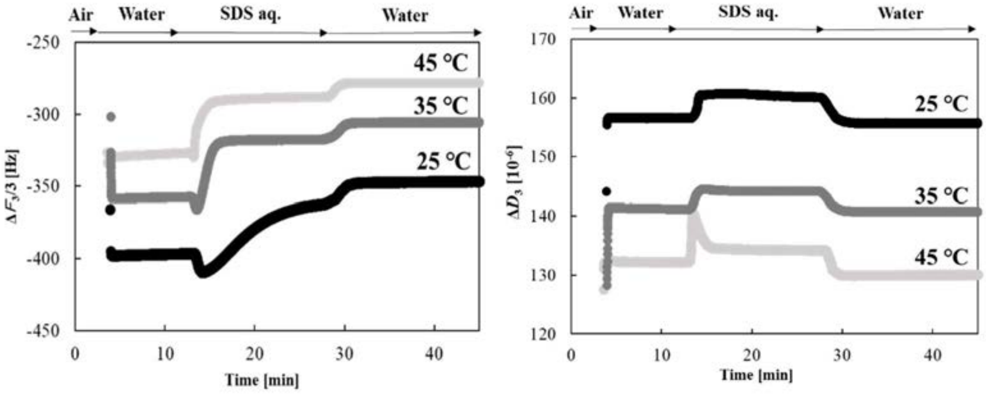

Fig 1. Typical QCM-D results for the SDS – $C_{16:0}$ system, measured at different temperatures.

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Solid impregnation of organic waste from cutting fluids before immobilization in solid matrix

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The disposal of organic waste from cutting fluids can pose a significant environmental and economic burden on industries. One potential solution is the immobilization of the waste in a solid matrix, such as alkali-activated materials (AAMs), which can reduce its volume, mitigate its environmental impact, and potentially create value-added products. However, the immobilization process can be challenging due to the hydrophilic nature of the waste, which can make it difficult to mix uniformly with the matrix material. Moreover, hydrolysable nuclear waste can react with its containment environment. For example, vegetable oils undergo a saponification reaction when in contact with an alkaline matrix [1].

The solid impregnation method involves adsorbing organic waste onto mineral fillers with a high specific area. This technique is therefore a pre-treatment of the waste prior to immobilization in a solid matrix. The major benefit of using this method is that the organic liquid waste is adsorbed onto a solid substance at the beginning of the process and then added to the cement slurry as a solid material. As a result, the use of additional components like surfactants is typically not necessary, except if a surface modification of the particles – through grafting of surfactants – allows for an improvement in the wetting of particles [2]. Adding a solid material to a cement mixture is simpler than adding a liquid, and the characteristics of the resulting composite, particularly its mechanical performance, are anticipated to be less affected [3].

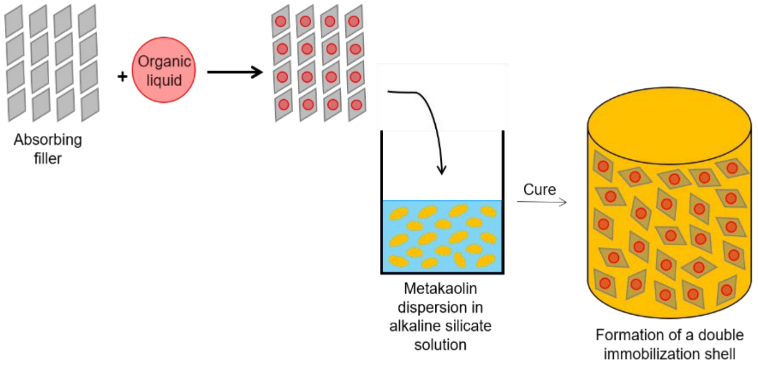

Fig 1. Illustration of the practical application of the solid impregnation method

In this study, different mineral fillers (bentonite, celite, sepiolite and metakaolin) were tested for impregnating two types of hydrolysable organic waste: vegetable oil and tributyl phosphate. To achieve this, optical microscopic observations, rheological tests, particle size, zeta-potential, and contact angle measurements were performed. The organic liquid/mineral filler ratio was optimized to impregnate the maximum amount of organic liquid possible, and the addition of surfactants on the particle surface increases this ratio.

The results show that impregnation on sepiolite is a promising pre-treatment method for incorporating organic waste into an immobilization matrix without leaching.

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Understanding the nuclear waste management of organic compounds from cutting fluids with a chemical and formulation perspective

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In industrial cutting processes, cutting fluids (CFs) – also called metalworking fluids – are often used to lubricate and cool down the cutting fluids. The formulation of CFs is a complex process that involves the careful selection and blending of various raw materials, such as base oils, additives, and emulsifiers, to meet the specific requirements of the cutting operation [1]. These fluids may contain organic compounds that can pose a risk to human health and the environment if not properly managed. The management of nuclear waste from organic compounds in CFs requires a chemical and formulation perspective to understand the complex nature of these products. and how they interact with the environment.

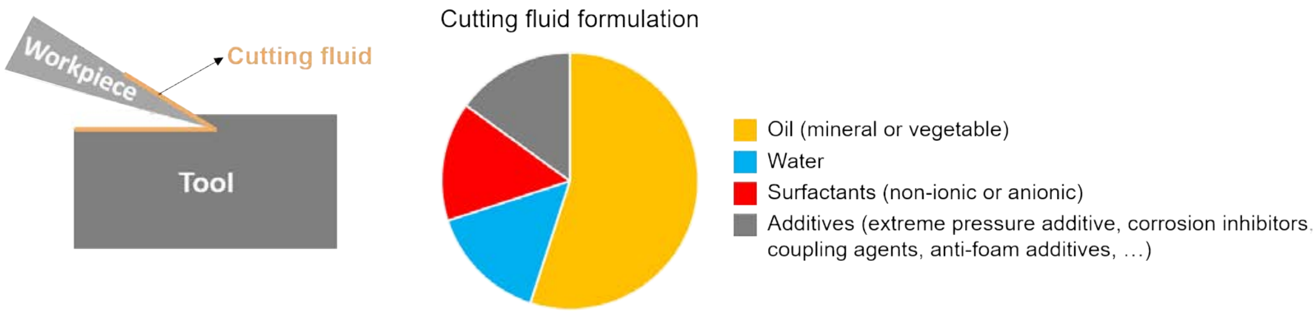

Fig. 1. Illustration of the practical application of a cutting fluid and formulation of a semi-synthetic fluid

In recent years, there has been a growing emphasis on the development of CFs that are environmentally friendly and sustainable. Even though mineral oils represent 85% of the cutting fluids on the market in 2005, mineral-based CFs tend to be replaced by vegetable-based CFs. Indeed, vegetable oils are known for their low toxicity, their biodegradability and the fact that they constitute a renewable resource. When they are used for cutting operations in nuclear power plants, these fluids have a potentially radioactive character and cannot be treated like other conventional waste. Alkali-activated materials (AAMs) have emerged as a promising alternative to traditional Portland cement for a range of applications. They are produced by mixing an alkali activator with a precursor material, such as clay, to form a solid matrix [2]. In recent studies, the potential of AAMs as a matrix for the disposal of nuclear waste has been explored. AAMs have been shown to have excellent mechanical properties, high durability, and resistance to leaching, making them ideal for use in long-term storage applications.

Some organic compounds with reactive chemical sites (esters, carboxylic acids, etc.) undergo a hydrolysis reaction in contact with AAMs. This is the case, for example, of vegetable oils [3].

This study aims to provide an overview of the current understanding of nuclear waste management of organic compounds from cutting fluids. It explores the properties of cutting fluids, the different types of organic compounds that may be present, and the potential risks associated with their disposal. A chemical and formulation perspective is applied to provide a comprehensive understanding of the behavior of organic compounds.

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Biocompatible and amphiphilic poly(2-oxazoline)s: Towards a new gold standard for cosmetics?

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Over the past few decades, polyoxazolines (PAOx) have gained renewed interest as a potential alternative to traditional polyethylene glycol ethers (PEGs) due to their high biocompatibility, low toxicity, and greater tunability. In recent times, block and gradient PAOx based on 2-methyl-2-oxazoline and 2-phenyl-2-oxazoline as hydrophilic and hydrophobic comonomers, respectively, have demonstrated significant emulsifying properties at low concentrations. This class of pseudo-polypeptide has been tested on model systems without electrolytes or complex oil mixtures and has shown excellent emulsifying properties with good rheological properties. However, their performance in real applications, i.e. for complex formulations, remains unexplored.

Therefore, this study aimed to investigate the emulsifying properties of PAOx in real cosmetic products by formulating a series of various PAOx-stabilized products, such as neutral cream, scented hand cream, anti-aging cream, BB cream, sunscreen, depilatory cream, and anti-acne cream. The goal was to assess the influence of the presence of fat-soluble active ingredients, pigments, fillers, or high pH conditions on the physical-chemical characterization of PAOx-stabilized emulsions. Systematic granulometry, stability, and rheology studies were performed.

The results showed that PAOx could stabilize all formulated products durably without the need for co-surfactants. In some cases, the concentrations required to achieve the same level of physicochemical performance were found to be ten times lower than the reference formulations. For some formulations, PAOx also acted as a multi-task raw material and provided similar rheological properties as the thickening agents, thereby reducing the need for additional additives. Lastly, gradient copolymer-stabilized emulsifiers demonstrated similar performance to block copolymer counterparts, offering a new platform of biocompatible and high-performance emulsifiers for the cosmetic industry through a one-step statistical copolymerization process.

CeO_2-based peelable gel for neutralization and skin decontamination toward chemical warefare agent simulants.

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CONTEXTE: Accidents with toxic industrial chemicals and threats posed by chemical warfare agents, as organophosphorus nerve agents and blistering agents, has become an increasing concern over the last decades. Intoxication is not only due to inhalation but dermal route can also be important and can quickly lead to death. It is therefore crucial to have suitable means of personal protection and decontamination and even if some are already commercially available they often present drawbacks. Efforts have therefore been made to develop new systems and several studies have shown the interest of metallic nanoparticles (NP). In this study, we demonstrated the interest of CeO_2 NP for the degradation of organophosphorus and in a second step, a peelable gel incorporating CeO_2 NP has been developed for efficient skin decontamination.

METHODS: A simulant warfare agent (Paraoxon, POX) was used is the study. CeO_2 NP with different size or shape were synthetized, characterized and their *in vitro* degradation properties towards POX evaluated. In a second step, a peelable gel incorporating CeO_2 NP has been developed for efficient skin decontamination. The formulation has been optimized through design of experiments and its properties characterized. Its efficiency towards neutralization and skin decontamination of POX has been evaluated *in vitro* and *ex vivo* on Franz cell with pig skin.

RESULTS AND DISCUSSION: We demonstrated the influence of CeO_2 NP size, morphology and crystallographic planes on the degradation of paraoxon, with a higher activity of the {111} facets as compared to the {100} facets, or ill-defined surface. Nano-octahedra CeO_2 NP appeared particularly promising for the degradation of POX and were then incorporated to a gel. It has a continuous thick consistency and can be applied to the skin, allowed to dry in few minutes and then peeled off. Even after incorporation to the gel, NP retained their neutralization properties *in vitro*. The interest of the peelable gel for neutralization and skin decontamination was clearly demonstrated *ex vivo* on Franz cell with a decrease by about 5 of the quantity of POX absorbed into the skin and a decrease of 3 to 4 in the viable skin which was much higher than the use of cotton or CeO_2 NP as powder.

CONCLUSION: Efficient CeO_2 NP were designed and evaluated for phosphorous agent degradation. A peelable gel incorporating CeO_2 NP has also been developed for efficient skin decontamination against toxic chemicals while being designed to be safe to use on skin, retaining the promising properties of CeO_2 NP, easy to handle and adapted to the context of application (battlefield or civil exposure).

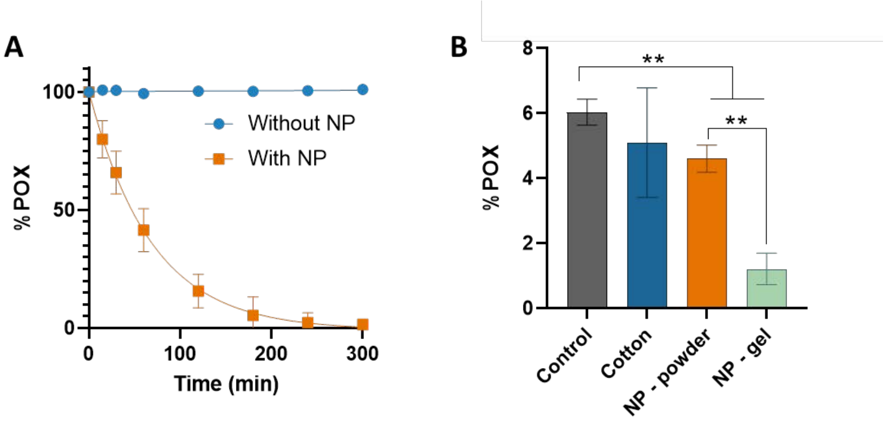

Fig 1. A) Degradation properties of nano-octahedra CeO_2 NP towards POX in water. B) Skin decontamination efficiency of nano-octahedra CeO_2 (NO) on Franz cells. Representation of the % of POX absorbed into the skin, 24h after decontamination.

Facilitated Hydrotropy of a Promising Anti-stacking Agent: Phloroglucinol

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Polyphenols are natural molecules with many potential health benefits [1], but poorly water-soluble despite having several hydroxyl groups. One reason is that numerous polyphenols exhibit strong π-stacking, resulting in the formation of highly hydrophobic aggregates formed through interactions between the aromatic rings of the polyphenols. π-stacking is a particularly significant phenomenon in biology, influencing the self-aggregation of proteins. In solution chemistry, π-stacking plays a major role in the solubilization mechanisms of many natural molecules. Strong stacking tends to limit significantly the solubility of aromatic molecules. Therefore, the use of compounds able to break this aggregation ("anti-stacking agents") would greatly favor their solubilization.

Phloroglucinol (benzene-1,3,5-triol) is one of the oxidation by-products of many flavonoids [2]. It results from the degradation of phloroglucinic acid. In the context of the observed enhanced solubility of certain flavonoids with autoxidation degradation, phloroglucinol was investigated as a potential hydrotrope for native flavonoids, particularly those that exhibit a strong stacking, i.e. quercetin and morin. It was compared to pyrogallol, another benzene-triol, which is already recognized as a hydrotrope in the literature [3].

As phloroglucinol lacks the required high aqueous solubility to perform on its own as a strong hydrotrope, facilitated hydrotropy techniques were used to boost its action. Ethanol/ water binary mixtures and the addition of pyrogallol were tested in this regard. It has been observed that the system phloroglucinol/ pyrogallol exhibits a synergetic effect on the solubilization of quercetin.

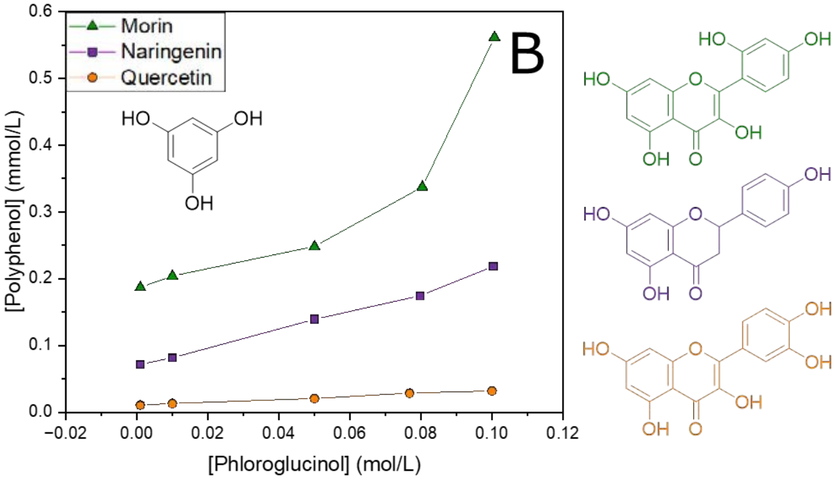

Fig 1. Solubility profiles of studied polyphenols in water with phloroglucinol. Purple: naringenin. Orange: quercetin. Green: morin

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Enhancement of Water Solubilization of Quercetin by Meglumine and Deprotonation Order Determination Method with COSMO-RS

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Quercetin is a well-known flavonoid, a natural molecule found in many plants, fruits, and vegetables, with numerous health benefits [1]. Like other polyphenols, quercetin is very poorly water-soluble. One way to enhance this solubility without co-solvent or complex structuration is to increase the pH to form polyphenates, but it often leads to oxidation of the compound and does not suit biological applications (physiological pH = 7.4).

The addition of meglumine, an aminocarbohydrate derived from glucose, was found to be able to enhance the water-solubility of quercetin among other polyphenols, at any given pH value from approximately one unit above the first pKa [2]. A compromise was found between solubility enhancement and reasonable stability against oxidation for quercetin at pH 8.

The solubilization mechanism is believed to be a proton exchange between the hydroxyl groups of quercetin and the amine group of meglumine, resulting in a salt formation. Hydrogen bonding of water molecules with the hydroxyl groups of meglumine brings hydration and enables the breaking of the π-stacking of quercetin. In this regard, one crucial parameter to consider is the order of deprotonation of the hydroxyl groups of quercetin and its pKa values. Since the latter are particularly challenging to measure due to quick oxidation, there is no real agreement in the literature. Thus, we developed a method based on pKa calculation with COSMO-RS software for every possible combination of deprotonation states of quercetin [2].

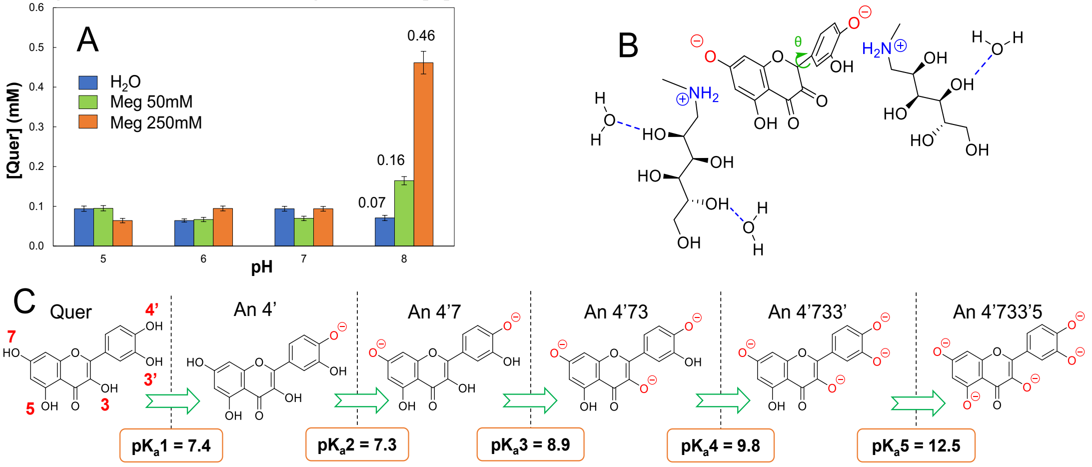

Fig 1. Solubilization of quercetin as a function of pH and meglumine concentration (A), schematic representation of solubilization mechanism (B), and determined deprotonation order of quercetin (C).

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Identification and unravelling of industrial and artists' alkyd paints and their reticulation using chemical depolymerization and ultra-high resolution mass spectrometry

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Alkyd paints, also known under the name of glycerophthalic paints, are oil-modified ester resin introduced in the late twenties, obtained by the reaction of a polyol, the most common being pentaerythritol, and a polyacid, commonly (iso)phthalic acid, which is then further esterified by a traditional siccative oil (linseed, safflower, poppy or walnut oil). As they are mostly based on natural products, there is a growing interest in alkyd paints. Despite deriving from traditional oil paint and thus having the same siccativation mechanism, alkyd paints present a more varied composition, which makes their analyses even more complex. This work proposes an innovative derivatization method for the analysis of both fresh and polymerized artists' alkyd paint samples by means of chemical depolymerization and ultrahigh resolution mass spectrometry. For art paintings, the sensitivity is down-to-the-order-of-micrograms.

We started by studying present-day artists' or industrial paints using 1D and 2D NMR, showing the great variability of alkyd paints compared to traditional oil paints. DOSY NMR spectroscopy highlighted that the alkyd binder is composed of two different parts: the alkyd resin and the siccative oil. Using LC-NH2 columns the two components in paint tube extracts were successfully separated and individually analyzed by FT-ICR MS and NMR. We extended this study to industrial paints covering paint samples ranging from in between the two World Wars, the fifties, the sixties to presentday. In particular we studied the French brand Ripolin™, presumably used by Picasso. After transamidation and polyalcohol derivatization, phthalic (or isophthalic) acid, pentaerythritol and the common fatty acids coming from triglycerides were found in both fresh and siccativated paints sampled at different ageing stages. In polymerized paints, signals in the high m/z region, corresponding to crosslinked structures, were classified using Kendrick and Van Krevelen plots in order to distinguish the nature of the crosslinking bonds. In the low *m/z* region, oxidation and degradation products as aldehydes and carboxylic acids were identified. The comparison between fresh, one-week polymerized, or one-year polymerized paint samples showed the progressive disappearance of polyunsaturated fatty acids (i.e., linolenic and linoleic acid) and the appearance of oxidation products (e.g., hexanal, sebacic acid, azelaic acid, ...) and crosslinks between unsaturated fatty acid either by C-C or C-O-C bonds. Moreover, pigments have a strong effect on the formed polymeric network: they may either favour the polymerization reaction (Chromium, Cobalt, Iron salts) or inhibit it (alizarine red, a polyphenol antioxidant). Moreover, in the high m/z range we identified markers leading back to the formulation of the paint tube for some brands as Winsor&Newton's Griffin™ or Gamblin Fastmatte™ alkyd. Examples of artist's painting analysis on microscale sampling will be presented.

Synthesis of a hyperbranched polyglycerol terminated with itaconate groups as novel crosslinking agent for hydrogels

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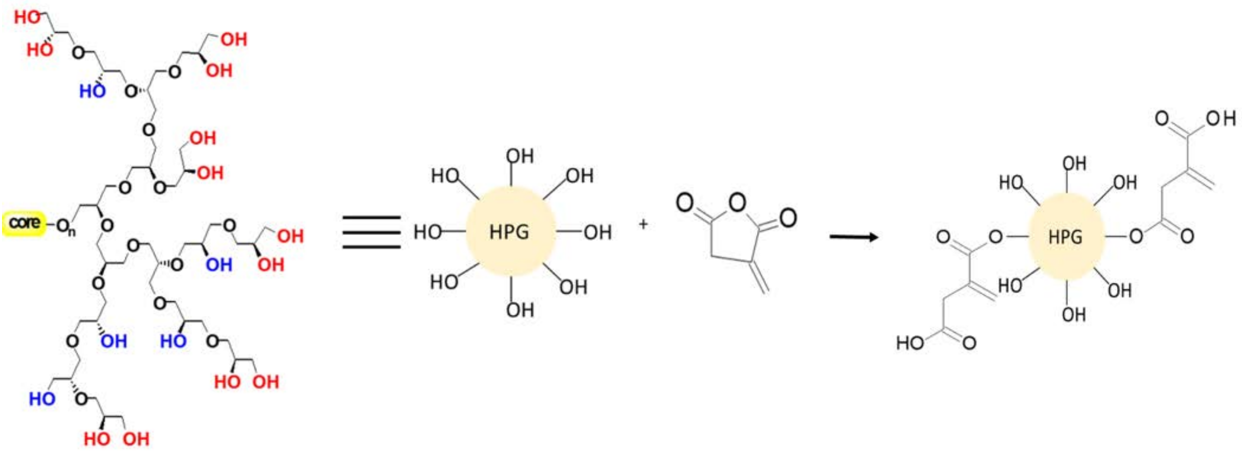
Novel crosslinkers are important molecules for developing hydrogels with specific properties. Herein hyperbranched polyglycerol has been synthesized by a controlled ring opening anionic multibranching polymerisation and further functionalized by an esterification reaction with itaconic anhydride (HPGf). The HPGf crosslinking molecules display numerous and controllable amounts of terminal itaconate functions, which can crosslink through a radical reaction, giving soft, pale yellow and transparent materials. This study demonstrate that side reactions take place during the functionalization giving itaconate function but also less reactive citraconate functions. The use of an increasing quantity of an acid catalyst was shown to increase the ratio of itaconate up to more thant 99%. This research work demonstrates a new way to synthesize a biocompatible crosslinker for hydrogels.



Temperature-responsive Pickering Emulsions Stabilized by Poly(Ethylene Glycol)-Functionalized Silica Particles

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Particle-stabilized emulsions, also called Pickering emulsions, are more stable than conventional emulsions. Pickering emulsions may be useful for reducing the surfactants amount and so, the risk for health and environment. Although a long-term stability is generally the final aim of a formulation process for food, cosmetics, paints, etc., a transitory stability (*i.e.* on demand destabilization) might be wanted for other applications such as emulsions polymerization, oil recovery or catalyst recovery in order to collect the product of interest. In these cases, additional disruption mechanisms need to be introduced to achieve the destabilization of the system, which may increase the costs and the energy consumption.

Polyethylene glycol (PEG) is a water-soluble and temperature-responsive polymer. The temperature increase induces a modification of the conformation of the polyoxoethylene chains (from polar to nonpolar due to dehydration of the ethylene oxide units). Surface active particles are more attractive than surfactants since they form much more stable emulsions. The use of PEG adsorbed onto the silica surface may induce the release of some PEG molecules in one of the two phases when the emulsion is destabilized. One way to overcome this issue is to covalently bind the PEG onto the silica NPs.

Herein, we report on the elaboration and characterization of temperature-responsive Pickering emulsions stabilized with PEG-functionalized silica particles. The particles were prepared through a one-step synthesis based on the hydrolysis and condensation of the silica precursor in the presence of PEG. The physicochemical properties of the NPs have been thoroughly characterized before the preparation of emulsions. We find that PEG-functionalized silica particles form temperature-responsive Pickering emulsions with oils of different nature. These emulsions undergo a clear temperature-triggered destabilization when heated.

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Light-driven Pickering interfacial catalysis for the oxidation of alkenes at near-room temperature

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In this study, we have developed an emulsion system combining plasmonic Au-loaded amphiphilic silica nanoparticles ($Au/SiO_2–C_3$) and tri(dodecyltrimethylammonium) phosphotungstate ($[C_{12}]_3[PW_{12}O_{40}]$) nanoparticles acting as an on-site photoassisted heater/activator and a catalyst, respectively, at the water/oil interface. The system exhibits a 5-fold increase of activity compared to the thermal reaction for the near-room temperature oxidation of alkenes with H_2O_2. The nanoparticles show excellent recyclability and structural stability. This study opens an avenue to design multiphase photoreactors for oxidation reactions at mild temperature, with a potential energy saving of 74% compared to that of thermally heated reactors at isoconversion.

References

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Emulsions stabilized by polydopamine particles

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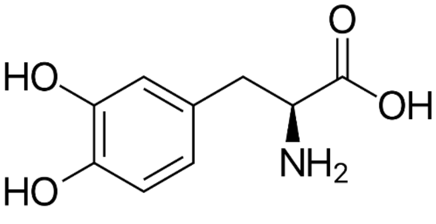
Particle-stabilized emulsions, known as Pickering emulsions, exhibit superior stability compared to conventional emulsions. These emulsions offer the potential to reduce the amount of surfactants used, thereby mitigating health and environmental risks.

Polydopamine (PDA) has attracted significant attention for its ability to coat various materials without prior surface treatment. Similar to the proteins produced by mussels, PDA possesses strong adhesion properties to diverse surfaces, including wet surfaces, thanks to the presence of catechol groups. PDA is derived through the polymerization of dopamine under basic pH conditions, allowing for a simple process in either aqueous or organic phases.

In this study, we conducted an investigation into the formulation of emulsions stabilized with PDA particles, examining the influence of different parameters such as PDA concentrations, oil-to-water ratio, and the type of oil used.



3,4-dihydroxyphenylalanine
(DOPA)