



Book of Abstracts

Agenda

- Zsigmondy Poster



Name	Abstract
Basseem Radwan	Supramolecular Functionalization of Janus Droplets for Biosensing of Cyanurates and Barbiturates
Frederic Finke	Synergisms of enzyme additive mixtures for solid fat removal
Jonathan Garthe Korin Gasia Ozkaya & Ramanujam	SANS investigation of the effect of end groups in linear PNIPAM homopolymers Soft Matter Research at LCMCP, Sorbonne University, Paris: Techniques, Applications and Perspectives
Philipp Hammers	Polydopamineacrylamide as a Dual-Functional Anchor for Iron Oxide and Gold Nanoparticles
Vahan Abgarjan	Influence of uniaxial compression on soft colloidal monolayers
Elias Hallenbach Joice Maria Scheibel	Structure formation of polymer brush/gold nanoparticle composite materials Galactomannan-based Hydrogel as a carrier for α -Bisabolol-loaded nanocapsules intended for biomedical application
Liu Tang	A sodium hyaluronate microneedle patch and conductive hydrogel integrated non-invasive transdermal insulin delivery platform via electrically driven controlled release.
Manuel Trömer	Ternary Microphase Diagram of SBM Triblock Terpolymers in Controlled Spherical Confinement
Angelita Rita Krama	Study of the phase behavior of Rhamnolipid and ethoxylated alcohol
Cara Kohler	Characterization of sophorolipids and study of synergism with cationic surfactants
Arshdeep Singh Bains Mohadeseh Bagherabadi	Improved Solubilization of Fragrances in Sugar Surfactant Solutions using Deep Eutectic Solvent (NADES)-Water Mixtures Peptide grafting into mesoporous silica for transport control, controlled release, and wound healing
Tim Stank	Exploring Thermal-Responsive Structural Changes in Unilamellar Phospholipid Vesicles Induced by Interaction with Di-Rhamnolipids
Yuzi Hong	Janus Droplet Liquid Sensing Platform with Automated Real-Time Morphology Monitoring
Moritz Stanek	Interfacial Properties and Phase Behavior of Mannosylerythritol Lipids and Mixtures with Anionic Surfactants
Semira Bener	Droplet Springs: Structuring liquids with programmable transience via interfacial jamming of pH-responsive block copolymers
Simone Schog	Structure of Microgels in Dense Monolayers
Julian Ringling	In-situ monitoring of core-shell microgel monolayers

Supramolecular Functionalization of Janus Droplets for Biosensing of Cyanurates and Barbiturates

Basseem Radwan¹ and Lukas Zeininger¹

¹ Department of Colloid Chemistry, Max Planck Institute of Colloids and Interfaces, Am Muehlenberg 1, 14476 Potsdam, Germany

Presenting author e-mail: basseem.radwan@mpikg.mpg.de

Keywords: Janus Droplets, Supramolecular Chemistry, Hamilton Receptors, Biosensing

Supramolecular chemistry presents a promising frontier in the development of advanced sensing systems with diverse applications [1]. This study focuses on leveraging biphasic Janus droplets, which exhibit remarkable sensitivity to their chemical surroundings, through intricate changes in the droplets' morphology, facilitating optical detection [2]. Our novel approach involves the functionalization of Janus droplets for the specific supramolecular-based detection of cyanurates and barbiturates, showcasing their potential in sensing and biosensing applications.

To achieve this, we employ tailor-made Hamilton receptor-based surfactants designed to exploit the high affinity of Hamilton receptors for target analytes, utilizing six hydrogen bonding interactions [3]. The asymmetric surface properties of Janus droplets offer controlled manipulation, providing distinct advantages for various applications [4]. Through a comprehensive approach involving experimental characterization and theoretical modeling, we anticipate elucidating the intricate mechanisms governing the interaction between Hamilton receptor-based surfactants and target analytes. These insights will contribute to the design principles for efficient sensing platforms.

Our work culminates in the practical utility of the functionalized Janus droplets for rapid and selective detection of cyanurates and barbiturates, demonstrating their capacity for the visualization and *in-situ* quantification of supramolecular host-guest interactions in complex aqueous environments. This research opens avenues for the development of advanced supramolecular sensing systems based on functionalized Janus droplets.

References

- [1] J.-H. Tian, H. Xu, X.-Y. Hu, D.-S. Guo, *Supramol. Mater.* **2024**, *3*, 100063.
- [2] L. Zeininger, *Anal. Bioanal. Chem.* **2023**, *415*, 5205–5219.
- [3] S. K. Chang, A. D. Hamilton, *J. Am. Chem. Soc.* **1988**, *110*, 1318–1319.
- [4] L. D. Zarzar, V. Sresht, E. M. Sletten, J. A. Kalow, D. Blankschtein, T. M. Swager, *Nature* **2015**, *518*, 520–524.

Synergisms of enzyme additive mixtures for solid fat removal

Frederic Finke^{1,2}, Christoph Bayer^{1,3}, Amit Tewari⁴, Peter Schmiedel⁵, Arnd Kessler¹ and Guillaume Delaittre²

¹Henkel AG & Co. KGaA, GRR Smart Washing Technology, Düsseldorf, Germany

²University of Wuppertal, Organic Functional (Macro)Molecules, Wuppertal, Germany

³University of Duisburg-Essen, Institute of Technical Chemistry, Essen, Germany

⁴Henkel AG & Co. KGaA, GRR Applications & New Bio Concepts, Hamburg, Germany

⁵Henkel AG & Co. KGaA, GRR Physical Chemistry, Düsseldorf, Germany

Presenting author e-mail: frederic.finke@henkel.com

Keywords: solid fat, enzyme, sustainability, low temperature

The effect of both chemistry and temperature in cleaning processes is critical to the removal of solid and liquid fats from substrates. While liquid fats are removed by forming emulsions, solid fats must first be melted at high temperatures ($T > 50^{\circ}\text{C}$) to be emulsified. [1] However, this process requires a considerable amount of energy to heat the cleaning liquid, which is not sustainable. Therefore, new ways to remove solid fats at low temperatures ($T < 30^{\circ}\text{C}$) are needed. Lipase catalysed fat hydrolysis, which is well known from the literature, is used for this purpose. [2] This approach is extended by the addition of sustainable materials to promote the removal of solid fats in a sustainable manner.

In this work, the desorption of solid fats was studied using the quartz crystal microbalance with dissipation monitoring (QCM-D). It was found that the characteristic time required for solid fat desorption is significantly reduced when sustainable materials are added. As a result, sustainable materials can be considered as a sustainable alternative to traditional cleaning components.

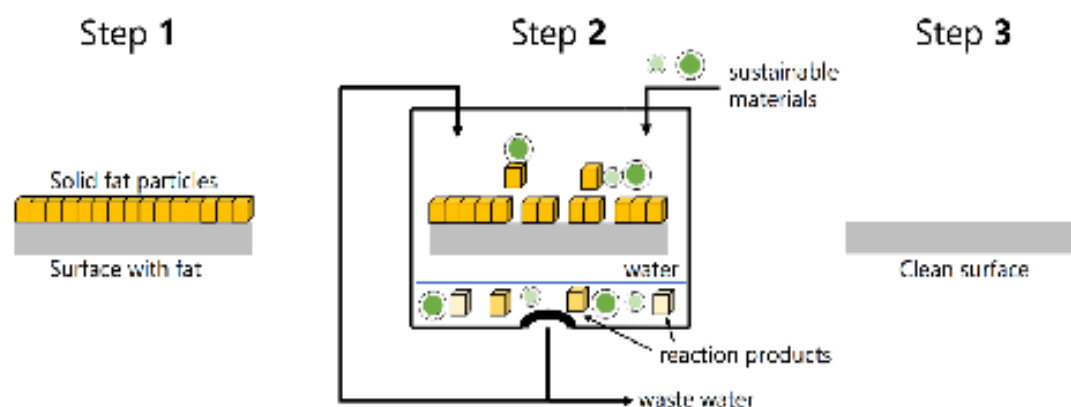


Figure 1. Schematic of enzymatic removal of solid fat using sustainable materials.

References

[1] E. Smulders et al.: "Laundry Detergents", Wiley 2002.

[2] T. Snabe, S.B. Petersen, Lag phase and hydrolysis mechanisms of triacylglycerol film lipolysis, *Chemistry and Physics of Lipids*, 2003, 125, 69-82, [https://doi.org/10.1016/S0009-3084\(03\)00072-0](https://doi.org/10.1016/S0009-3084(03)00072-0).

SANS investigation of the effect of end groups in linear PNIPAM homopolymers

Jonathan Garthe¹, Kristina Wagner¹, Matthias Karg¹

¹*Institut für Physikalische Chemie I: Kolloide und Nanooptik, Heinrich-Heine-Universität
Düsseldorf, 40225 Düsseldorf, Germany*

Presenting author e-mail: jonathan.garthe@uni-duesseldorf.de

Keywords: Small-angle neutron scattering, PNIPAM, Homopolymer, End group effect

Responsive polymers, such as poly(*N*-isopropylacrylamide) represent an exciting material class with a wide range of applications for example as phase-change materials, actuators and self-healing systems. In the last decades, the behavior of thermoresponsive polymers with a lower critical solution temperature (LCST) has been thoroughly studied via a variety of methods including small-angle neutron scattering (SANS).[1] For such polymers, recent works found the existence of polymeric micelles, when the polymers possessed hydrophobic end groups.[2] It was found that the internal structure of these polymeric micelles depends on the molecular weight of the polymer as well as on the type of end group.

Therefore, we attempt to investigate the solution behavior and the occurrence of micelles as a non-dominant phase. In this work, we use RAFT polymerization to synthesize linear PNIPAM chains with a low dispersity that are terminated with an aliphatic dodecane chain terminus. For a direct comparison, we also investigate the same polymers after cleavage of the hydrophobic end groups. We analyze the polymers using surface tension measurements to determine the critical micelle concentration of the polymers (Figure 1, left). Additionally, we use dynamic light scattering in dependence of the polymer concentration to determine the size of potential aggregates that form (Figure 1, inset). To further resolve the overall dimensions, as well as to determine the volume fraction of these aggregates we use SANS (Figure 1, right). This also allows us to determine the aggregation number of these micelle-like structures in dependence of the end group and overall polymer concentration.

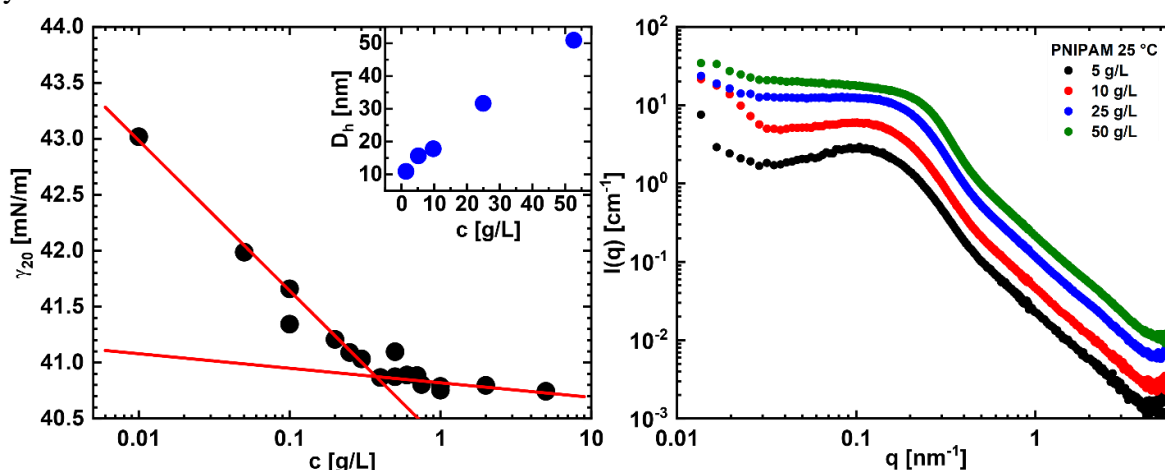


Figure 1. Left: Determination of the CMC via concentration-dependent surface tension measurements. Inset: Hydrodynamic diameter determined from DLS as a function of polymer concentration. Right: SANS data of linear PNIPAM (20 kDa) at different concentrations.

References

- [1] Lerch, A.; Käfer, F.; Prévost, S.; Agarwal, S.; Karg, M.; *Macromolecules* 2021, 54, 7632- 7641.
[2] Fitzgerald, P. A.; Gupta, S.; Wood, K.; Perrier, S.; Warr, G. G. *Langmuir* 2014, 30, 7986-7992.

Soft Matter: Applications and Perspectives

Introduction

Research in synthetic and biological macromolecules, colloids, amphiphilic systems or membranes are the realm of so-called “soft matter”. LCMCP has an historical affinity towards soft matter research, but classically in association to inorganic systems. More recently, new research topics, carried out by both former and new members, focus more and more on soft systems as such. The goals are multifold, spanning from better understanding to soft materials development. The expertise of SMILES, that is crossing top-bench across scale and time techniques, reveals to be particularly useful.



Solid state NMR as a non destructive method for aging analysis of EPDM

Applications

Actual end-of-life criteria → tensile test → Towards a criterion based on solid-state NMR ?
→ Non-destructive ∝ m ∝ ∞ method
→ Less costly (little material / no cable removal)

- Analyse the evolution of the **network topology** during aging (^1H T_2 relaxation functions & ^1H double-quantum build-up curves)
- Correlation with mechanical tests

T_2 (^1H) relaxation function for an amorphous elastomeric network above T_g

Industrial elastomer blends: study of the cross-linking mechanisms

Applications

Network topology

- Elastically-active chains
- Crosslinks
- Entanglements
- Dangling chains
- Extractibles

Bulk organization by solid-state NMR

T_1 (^1H) measurements

- Number of phases
- Domain size estimation

Cross-link density distribution by solid-state NMR¹

^1H Double-Quantum coherence build-up curve

Selective description of the cross-linking behavior within both phases of elastomer blends

Self-assembled Hydrogels

Fibrillation and metallogel formation induced by metal salts.

Stabilization of green colloids cellulose nanocrystals

Water remediation

Biosurfactants as flocculating agents for heavy metals.

Biomimetic membranes

Incorporates biological elements or borrow concepts, ideas or inspiration from biological systems.

Functionalization of Phospholipid membranes

Stimuli
pH
Melting temperature
Permeability
Bending rigidity
Area per molecule etc.

Nanomaterials

Ag nanoparticles and nanowires synthesized in biosurfactant hydrogels upon reduction of Ag^+ centers.

Formulation

Replace conventional surfactants like SLS in industrial formulations for consumer products.

Petrochemical surfactant (SLS)

Compare and enhance biosurfactants properties : **viscosity, foaming, optical properties..**

Example of application as detergent in home and personal care : solubilization by micelles.

Cytocompatibility & biomedical applications

Use of novel molecules in regenerative medicine applications.

Low dosage could have beneficial effects, for example in skin regeneration & wound healing.
High dosage could have a potential effect as novel cancer treatments.

References

- Saalwächter, K and al. *The Journal of Chemical Physics*, **2003**, 119, 3468–3482
- Pubellier P., *Influence de charges micrométriques sur le vieillissement de composites à matrice polymère*, PhD Thesis, **2017**
- Poirier A. et al. *ACS Sustainable Chem. Eng.*, **2022**, 10, 50, 16503–16515
- Poirier A, Ozkaya K. et al. *J Surfact Deterg.* **2023**, 26(2):175-84.
- Poirier A. et al., *Soft Matter*, **2023**, 19, 378-393

Polydopamineacrylamide as a Dual-Functional Anchor for Iron Oxide and Gold Nanoparticles

Philipp Hammers¹, Jacob J. Nachtwey², Laura Hartmann^{2,3} and Matthias Karg¹

¹ *Physikalische Chemie I: Kolloide und Nanooptik, Heinrich-Heine-Universität Düsseldorf*

² *Institut für Organische und Makromolekulare Chemie, Heinrich-Heine-Universität Düsseldorf*

³ *Institut für Makromolekulare Chemie, Albert-Ludwigs-Universität Freiburg*

Presenting author e-mail: hammerp@hhu.de

Keywords: Ligand Exchange, Nanoparticles, Polymers, Superparamagnetism, Hyperthermia

Superparamagnetic iron oxide nanoparticles (SPIONs) and gold nanoparticles (AuNPs) are known for their hyperthermia capability in diagnostic imaging and cancer therapy due to their unique magnetic and optical properties, respectively.[1] To use their full potential, stabilizing ligands are necessary to prevent aggregation and enable biocompatibility. Typically, SPIONs are stabilized with oleic acid, a hydrophobic ligand, while AuNPs are stabilized with citric acid, which is a weak ligand for AuNPs.[2] For water-based applications, transition to a hydrophilic, long-term stable ligand is necessary.

Here, we present versatile and stable ligands derived from dopamineacrylamide for both systems with different anchoring motifs.[3] Polydopamineacrylamide (PDAAM) ligands are synthesized by RAFT polymerization with thiol end groups to attach strongly to AuNP surfaces, whereas hydroxyl groups of the catechol are used to attach to the SPION surface.

Successful ligand exchange is indicated by a phase transfer of particles from organic to aqueous phase and characterized by Fourier-transform infrared spectroscopy (FT-IR), ζ -Potential measurements and small-angle X-ray scattering (SAXS), as well as transmission electron microscopy (TEM) to verify the uniformity of shape and size of particles.

In addition, the thermal cleavage of acetonide protecting groups on catechols is investigated by irradiating AuNPs with near-infrared radiation (NIR), to regain the adhesive capabilities of dopamine in a fast and catalyst-free approach.

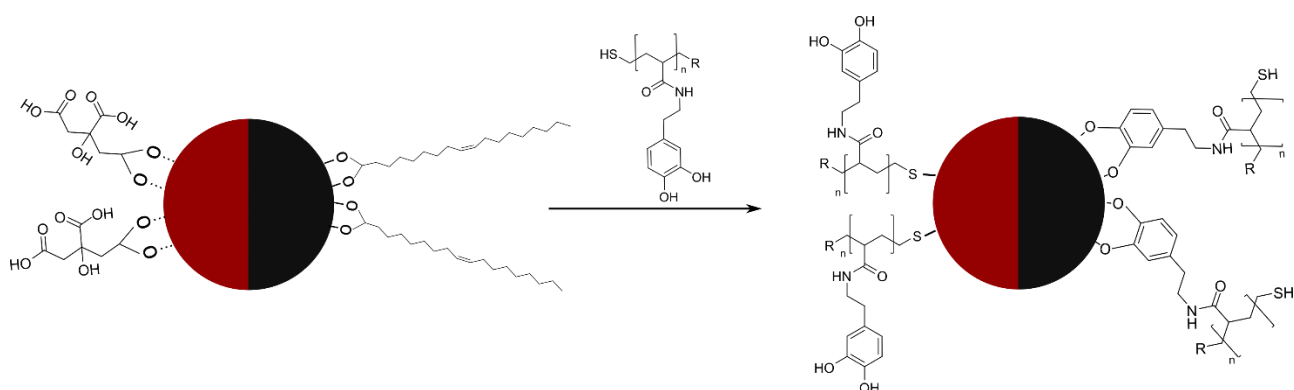


Figure 1. Schematic illustration of the bifunctional ligand exchange with PDAAM on AuNPs (red) and SPIONs (black).

References

- [1] Laurent, S., Dutz, S., Häfeli, U.O., Mahmoudi, M., *Adv. Colloid Interface Sci.*, 2011, 166, 8-23
- [2] Honold, T., Karg, M., *Langmuir*, 2017, 33(1), 253-261
- [3] Bonda, L., Schmidt, S., Hartmann, L., *Polymers*, 2023, 15(18), 3663

Influence of uniaxial compression on soft colloidal monolayers

Vahan Abgarjan¹, Keumkyung Kuk¹ and Matthias Karg¹

¹Physikalische Chemie I: Kolloide und Nanooptik, Heinrich-Heine-Universität, 40225 Düsseldorf, Deutschland

Presenting author e-mail: vahan.abgarjan@hhu.de

Keywords: colloidal monolayer, *in-situ* characterization, real-time investigation

The controlled assembly of molecules and colloids into two-dimensional structures has been a driving force in the advancement of surface functionalization techniques for nanocoatings and the development of functional materials. [1] The significance and comprehension of soft colloids have witnessed a notable surge in the past decade based on their characteristic soft properties and unique interfacial phase behavior. The Langmuir-Blodgett technique has emerged as a common method for investigating the assembly behavior of colloids at various interfaces, where their compression isotherms are systematically examined in terms of surface pressure (Π) as a function of interfacial area. Furthermore, structural insights regarding order and interparticle distances across different phases have been examined through complementary techniques such as atomic force microscopy, light microscopy, and small-angle x-ray/light scattering (SAXS/SALS). [2-5]

In previous investigations, our group studied various colloidal monolayers utilizing *in-situ* SALS implemented on a Langmuir trough (LT). [5] This study provided insights into structural development of colloidal monolayers in real-time. In the present study, we used micron-sized hard-core soft-shell microgels [6] and monitored the compression process and subsequent response of the monolayer using our *in-situ* setup (LT-SALS). We aim to emphasize and further discuss the outcome from previous investigations with a focus on compression parameters like speed and relaxation time.

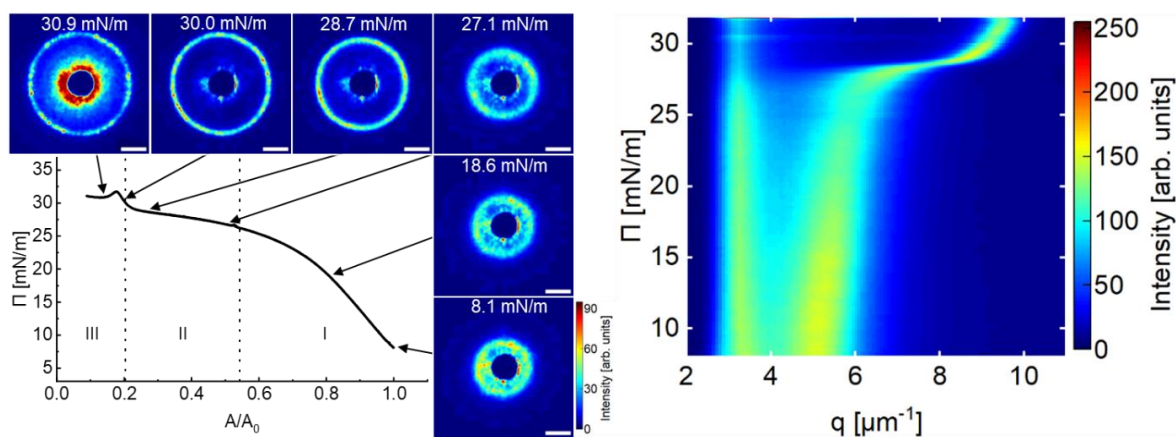


Figure 1. Left: compression isotherm (surface pressure Π against normalized area A/A_0) of a hard-core soft-shell microgel monolayer at the air/water interface with corresponding diffraction pattern from SALS at various Π . Scale bars correspond to 10 nm. Right: Connection of the radial profiles from SALS images (colour-coded intensity against the magnitude of the scattering vector q) with the corresponding Π .

References

- [1] O. N. Oliveira, L. Caseli et al., *Chem. Rev.*, 2022, 122, 6459-6513
- [2] A. C. Nickel, T. Kratzenberg et al., *Langmuir*, 2022, 38, 17, 5063-5080
- [3] M. Rey, M. A. Fernandez-Rodriguez et al., *Acc. Chem. Res.*, 2020, 53, 2, 414-424
- [4] C. Picard, P. Garrigue et al., *Langmuir*, 2017, 33, 7968-7981
- [5] K. Kuk, V. Abgarjan et al., *Soft Matter*, 2023, 19, 2, 175-188
- [6] K. Kuk, L. Gregel et al., *Gels*, 2022, 8, 516

Structure formation of polymer brush/gold nanoparticle composite materials

Elias Hallenbach¹, Philipp Ritzert¹ and Regine von Klitzing¹

¹*Institute for Condensed Matter Physics, Technical University of Darmstadt, Hochschulstraße 8, 64289 Darmstadt, Germany*

Presenting author e-mail: elias.hallenbach@pkm.tu-darmstadt.de

Keywords: composite materials, polymer brush, thin film, gold nanoparticles

Metal/polymer nanocomposites are versatile hybrid materials and find use in many fields such as photonics, biomedical engineering and catalysis. A promising realization of this type of hybrid material is the controlled self-assembly of gold nanoparticles inside the polymer brush, which induces color changes upon exposure to environmental changes enabling sensor applications. Therefore, we aim to gain insights into and control over the manufacturing process leading to more elaborate nanocomposite fabrication.

The polymer brushes in our model system serve as a matrix for the immobilization of gold nanoparticles (AuNPs). Particle uptake into the brush matrix is affected by parameters such as brush thickness, particle size and the brush grafting density^{[1][2]}. Polymer brushes are synthesized by Surface-Initiated Atom Transfer Radical Polymerization (SI-ATRP) directly from a silicon substrate. As has been shown earlier by our group, the grafting density has a strong impact on polymer-particle interactions (Fig. 1)^[2]. Therefore, the focus of this work is to evaluate synthesized Poly(oligo(ethyleneglycol)methacrylate) (POEGMA) brushes with varying grafting densities. Determination of the grafting densities is done by cleaving the polymers off the surface using Tetrabutylammoniumfluoride (TBAF). Polymer analytics yield a molecular weight distribution by which the grafting density can be calculated.

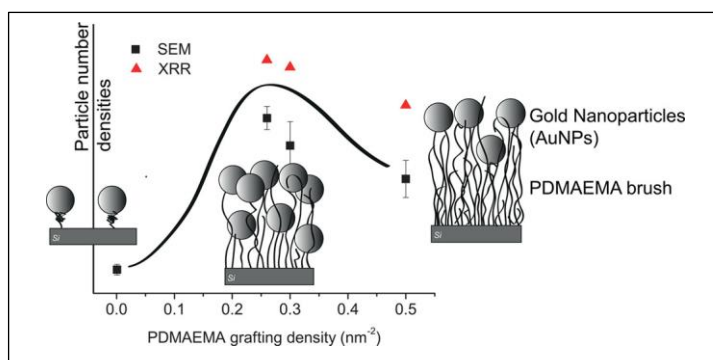


Figure 1. Particle number density of AuNPs in a Poly(2-(dimethylamino)ethyl methacrylate) (PDMAEMA) composite material. The particle number density is highest at intermediate grafting density (taken from [2]).

Acknowledgements: We acknowledge funding by the Deutsche Forschungsgemeinschaft (DFG) through GRK2516 (Grant No. 405552959).

References

- [1] S. Christau, S. Thurandt, Z. Yenice, R. v. Klitzing, *Polymers*, 2014 6, 1877-1896.
- [2] S. Christau, T. Möller, Z. Yenice, J. Genzer, R. v. Klitzing, *Langmuir*, 2014, 30, 13033-13041.

GALACTOMANNAN-BASED HYDROGEL AS A CARRIER FOR α -BISABOLOL-LOADED NANOCAPSULES INTENDED FOR BIOMEDICAL APPLICATION

Jóice M. Scheibel^{1,2}, Laiane S. da Silva¹, Daniela L. T. Schmitt², Thomas Hellweg¹, Karina Paese² and Rosane M. D. Soares²

¹Physical and Biophysical Chemistry, University Bielefeld, Bielefeld, Germany

²Federal University of Rio Grande do Sul (UFRGS), Porto Alegre, RS, Brazil

Presenting author e-mail: j.scheibel@wi-bielefeld.de

Keywords: Hydrogels; Nanocapsules; Galactomannan; α -bisabolol

According to the World Health Organization, burns cause more than 180,000 deaths annually worldwide. The skin, acting as a protective barrier against microbial invasion, is also extremely vulnerable to burns. This work aims to assess the physicochemical properties of galactomannan hydrogels, which incorporate α -bisabolol-loaded nanocapsules, for topical treatment of burn wounds. The methodology involved interfacial polymer deposition to prepare nanocapsule suspensions containing α -bisabolol.[1]. Five hydrogels were produced with 3 different concentrations of crosslinking agents (20, 40 and 60%).

The nanocapsules and formulations were physicochemically characterized with respect to average diameter, polydispersity, pH sensitivity, zeta potential, and rheological behavior before and after incorporation into semi-solid suspensions. The nanocapsule suspensions, containing 10 mg/mL of α -bisabolol, have an average diameter of $189 \text{ nm} \pm 4 \text{ nm}$ with a polydispersity index of 0.08 ± 0.03 . The hydrogel formulations were adjusted to exhibit an ideal pH of 4.85 ± 0.6 for cutaneous application, aligning with the typical pH range of healthy skin. The nanocapsules' negative Zeta Potential (ZP) values ($-8 \pm 1 \text{ mV}$ and $-18 \pm 4 \text{ mV}$) indicate stabilization via steric hindrance rather than electrostatic repulsion.[2] Furthermore, rheograms reveal non-Newtonian, pseudoplastic behavior (see fig. 1 right panel), characteristic of topical pharmaceutical formulations. In conclusion, these hydrogels maintain nanocapsule size stability and hold promise for burn wound treatment.

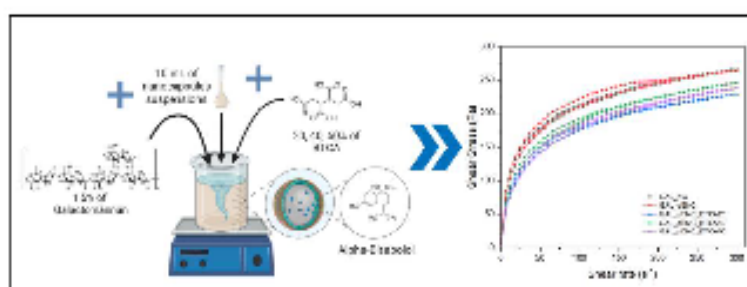


Figure 1. Left: Chemical structures of hydrogel-forming compounds. Right: Flow curve of crosslinked and non-crosslinked hydrogels.

Acknowledgements: The authors thanks CAPES and Bielefeld University for financial support.

References

- [1] Terroso, T. F., et al. *J. Drug. Deliv. Sci. Technol.*, 36 (2016): 99-109.
- [2] Paese, K., et al. *AAPS Pharm. Sci. Tech.*, 18 (2017): 212-223.

A sodium hyaluronate microneedle patch and conductive hydrogel integrated non-invasive transdermal insulin delivery platform via electrically driven controlled release.

Liu Tang¹, Gerhard Kalinka² and Michael Gradzielski¹

¹ *Stranski-Laboratorium für Physikalische und Theoretische Chemie, Institut für Chemie, Technische Universität Berlin, D-10623 Berlin, Germany*

² *Federal Institute of Materials Research and Testing (BAM), 5.3 Polymer Matrix Composites, Unter den Eichen 87, 12205 Berlin, Germany*

tangliu.tub@gmail.com

Keywords: microneedle arrays, conductive hydrogel, non-invasive, insulin and electrically driven.

Multiple daily subcutaneous injections of insulin present diabetic patients with constant pain, fear, and risk of infection [1]. We developed a transdermal drug delivery platform integrating dissolvable MNs based on a conductive hydrogel, which has multiple release kinetics of rapid passive release and electrically driven controlled release. Sodium hyaluronate (SH) is used as an excellent biocompatible material for dissolvable MN patches. By adjusting the concentration and molecular weight of SH, the MN patches showed good mechanical strength and puncture performance, while rapidly dissolving and releasing insulin after piercing the epidermis. This non-invasive insulin delivery method can not only effectively break the stratum corneum barrier, bypassing the gastrointestinal digestive system and avoiding first-pass effect to deliver large molecules drugs into the body [2], but also offers painlessness, convenience, safety and skin recoverability, significantly enhancing patient compliance. The conductive hydrogel is prepared by mixing quaternized chitosan grafted with polyaniline (QCSPA), polyvinyl alcohol (PVA) and borate (BA). This hydrogel undergoes dynamic cross-linking via borate ester groups and ionic interactions, resulting in conductive properties [3] and well-controlled viscoelastic properties. By adjusting the strength and duration of the electric field, the internal reticular structure of the hydrogel can be changed, leading to a variation in the dissolution rate and achieving the effect of controlled release [4]. Furthermore, the application of the electric field facilitates the subcutaneous transportation of charged drug molecules through electric drive, while the channels created by the MN arrays enhance the efficiency of iontophoresis to achieve a synergistic drug delivery strategy.

References

- [1] B. Z. Chen, L. Q. Zhang, Y. Y. Xia, X. P. Zhang, X. D. Guo, *Science Advances*, 2020, 6, eaba7260.
- [2] J. H. Jung, S. G. Jin, *Journal of Pharmaceutical Investigation*, 2021, 51, 503.
- [3] R. D. Pyarasani, T. Jayaramudu, A. John, *J Mater Sci*, 2019, 54, 974.
- [4] Y. Zhang, Y. Tan, J. Lao, H. Gao, J. Yu, *ACS Nano*, 2023, 17, 9681.

Ternary Microphase Diagram of SBM Triblock Terpolymers in Controlled Spherical Confinement

Manuel Trömer¹, Yorick Post¹, Elias M. Zirdehi², A. Nikoubashman³ and André H. Gröschel⁴

¹Center for Soft Nanoscience and Institute of Physical Chemistry, University of Münster

²Institute of Physics, Johannes Gutenberg University Mainz

³Leibniz-Institut für Polymerforschung Dresden e.V. and Institut für Theoretische Physik, TU Dresden

⁴Bavarian Centre for Battery Technology (BayBatt) and Bavarian Polymer Institute (BPI), University of Bayreuth

Presenting author e-mail: m_troe03@uni-muenster.de

Keywords: 3D confinement, DPD simulations, ternary microphase diagram, triblock terpolymers.

Combining Evaporation Induced Confinement Assembly (EICA) and the *Shirasu Porous Glass* membrane setup (SPG) is a viable method to produce size-tailored and internally structured polymer-based colloids with very narrow size distributions. In contrast to other emulsification methods such as e.g. vortex mixing, this type of cross-flow membrane emulsification is able to produce the emulsions in a controlled and more reproducible way [1, 2]. In the present study, we employ this approach on linear ABC triblock terpolymers to systematically study how their block compositions influence the morphologies of the resultant micro- and nanoparticles.

Experimentally we realize this by emulsifying organic solutions of polystyrene-*block*-polybutadiene-*block*-poly(methyl methacrylate) (SBM) triblock terpolymers with varying block compositions into aqueous solutions of sodium dodecyl sulfate (SDS). The emulsions are produced with the SPG-setup, so that we receive monodisperse and size tailored emulsion droplets. With the organic solvent evaporating over time, the polymer microphase separates and self-assembles into solid and internally structured micro- and nanoparticles. We systematically study the structures and morphologies of the obtained colloidal particles. In addition to using pure triblock terpolymers, we also alternate the compositions by blending homopolymer. Furthermore, the experimental findings are supported by DPD simulations.

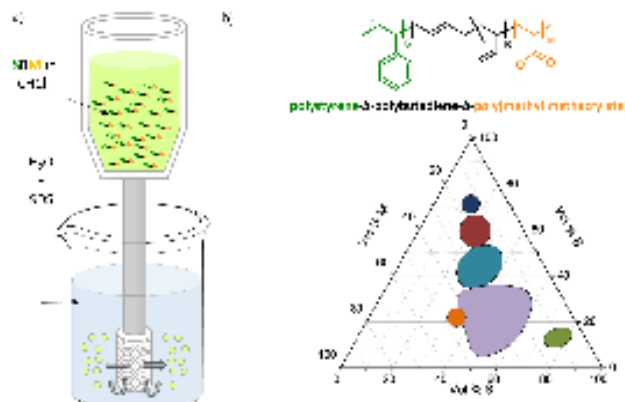


Figure 1. Schematic representation of SPG-membrane setup and ternary microphase diagram with different morphological regions indicated by different colors.

References

- [1] M. Trömer, E. M. Zirdehi, A. Nikoubashman, A. H. Gröschel, *Macromolecular Rapid Communications*, 2023, 2300123, 1.
- [2] S. Azhdari, Y. Post, M. Trömer, D. Coban, G. Quintieri, A. H. Gröschel, *Nanoscale*, 2023, 15, 14896.

Study of the phase behavior of Rhamnolipid and ethoxylated alcohol

Angelita Rita Krama^{1,2}, Cosima Stubenrauch¹ and Peter Schmiedel²

¹ Stuttgart University

² Henkel AG & Co. KGaA

Presenting author e-mail: angelita.krama@henkel.com

Keywords: rhamnolipid; C₁₂E₄; phase behavior; rheology.

Rhamnolipids (RL) are microbial biosurfactants with important industrial applications. RLs are glycolipids in which the amphiphilic structure is based on the presence of a hydrophilic head group consisting of one or two L-rhamnose units and a hydrophobic tail consisting of one or two β -hydroxy fatty acids [1, 2]. RLs are able to form worm-like micelles (WLMs) in the presence of ethoxylated alcohol-based nonionic surfactants [2]. These micelles form a viscoelastic network with typical rheological behavior [3]. The aim of this work is to investigate the phase behavior of a ternary system containing RL, ethoxylated alcohol (C₁₂E₄) and water at RL concentrations below 50%. To achieve this goal, a Design of Experiment (DoE) was performed. The samples were analyzed by oscillatory rheology, polarized microscopy and dynamic light scattering.

From the DoE, 98 samples were prepared with different concentrations of RL, C₁₂E₄ and water. The region of phase separation occurs at high concentrations of C₁₂E₄ and lower concentrations of RL. At high concentrations of ethoxylated the high repulsion between the surfactants due to their different structure and micelle shape, that is why it was observed a lamellar phase (L _{α}) formed by C₁₂E₄ and a micellar phase (L₁) formed by RL.

A typical rheological behavior for WLMs is to behave as a Maxwell's fluid, which means that it will behave as a viscoelastic fluid compared to micellar solutions, based on it is supposed to observe an increase in viscosity when WLMs are formed. Based on this hypothesis and using oscillatory rheology to determine the viscosity, it has been plotted a thermal ternary graph showing the variation of viscosity according to the different mixtures. It has been observed that there is a high viscosity at high concentrations of C₁₂E₄ showing a typical behavior for a L _{α} phase and it has been proved by polarized microscopy. An increase of the viscosity is also observed when the surfactant amount is above 25%, especially when RL /C₁₂E₄ ratio is smaller showing synergistic effect between them.

A final result was the hydrodynamic radius (R_h) of the samples. It was observed that the R_h increases as the ratio between RL and C₁₂E₄ decreases, it is an indication that larger micelles are formed when it is added the same amount of surfactants. However, additional studies such as microscopy (Cryo-TEM) and spectroscopy (SAXS) need to be performed to verify the shape of the micelles.

Reference

- [1] N. Baccile, C. Seyrig, A. Poirier, S. A.-d. Castro, S. L. K. W. Roelants und S. Abel, Self-assembly, interfacial properties, interactions with macromolecules and molecular modelling and simulation of microbial bio-based amphiphiles (biosurfactants). A tutorial review, " *Green Chemistry*", 23, 11, 3842-3944, 2021.
- [2] J. Birnbach, P. Schmiedel und M. Karg, Multi-component phase behavior of biosurfactants, " *Current Opinion in Colloid & Interface Science*", 68, 101765, 2023.
- [3] J. D. Peterson, W. Zou, R. G. Larson und M. E. Cates, Wormlike Micelles revisited: A comparison of models for linear rheology, " *Journal of Non-Newtonian Fluid Mechanics*", 322, 105149, 2023.

Characterization of sophorolipids and study of synergism with cationic surfactants

Cara Kohler^{1,2}, Janine Birnbach², Peter Schmiedel², Matthias Karg³ and Kerstin Hoffmann-Jacobsen¹

¹Hochschule Niederrhein, Krefeld, Germany

²LRS-Physical Chemistry, Henkel AG & Co. KGaA, Düsseldorf, Germany

³Heinrich-Heine-Universität, Düsseldorf, Germany

Presenting author e-mail: cara.kohler@henkel.com

Keywords: Biosurfactants, Sophorolipids, Catanionics

To reduce the dependency on crude oil and to create more biodegradable products, biosurfactants like sophorolipids can be used as substitutes for fossil-based surfactants in products. Sophorolipids exist in two different main forms, the acidic and the lactonic one. Due to their differences in their chemical structures their properties vary. Therefore, in this poster, the physico-chemical properties of pure acidic and pure lactonic sophorolipids as well their mixture are presented regarding their surface tension, cmc, phase behavior, interfacial tension, and foam behavior. Here, differences and synergistic effects between the two forms were found.

Furthermore, to increase the interfacial activity of the sophorolipid, the influence of various cations and cationic surfactants on the properties of the acidic sophorolipids were investigated. Depending on the type of cationic substance, synergistic effects were found with the sophorolipid and an enhancement of interfacial activity. These findings, especially regarding the synergism between the acidic sophorolipid and the cationic surfactant are an important step in enabling the commercial use of the sophorolipids.

References

- [1] Baccile, *Green Chem.* 23.11 (2021): 3842-3944.
- [2] N. Baccile, et. Al, Review in *Green Chem.* 23.11 (2021): 3842-3944
- [3] T. Joshi, et. Al, *Colloids Surfaces A Physicochem. Eng. Asp.* 260.1-3 (2005): 209-215
- [4] ISO 4311:1979: *Anionic and non-ionic surface active agents- Determination of the cmc* (1979)
- [5] M.J. Rosen, et.al, *Surfactants and Interfacial Phenomena*. New Jersey: John Wiley & Sons, (2012)

Improved Solubilization of Fragrances in Sugar Surfactant Solutions using Deep Eutectic Solvent (NADES)-Water Mixtures

*Arshdeep Singh Bains¹, Tomas Omasta¹
Anton Michel¹ and Michael Gradzielski¹*

¹Stranski-Laboratorium für Physikalische und Theoretische Chemie, Institut für Chemie, Technische Universität Berlin, Straße des 17. Juni 124, D-10623 Berlin, Germany

Presenting author e-mail: bains@tu-berlin.de

Keywords: solubilization, fragrances, NADES, sugar surfactant, terpenes

While traditional aqueous solutions are well-established for fragrance delivery [1], this study explores natural deep eutectic solvents (NADES) as a potential sustainable alternative. NADES offer several advantages over conventional organic solvents and ionic liquids, including biocompatibility and low cost [2].

Our investigation identified choline chloride-urea NADES (reline) as a promising candidate for fragrance solubilization due to its readily available and inexpensive components [2]. To further enhance fragrance solubility, we explored sugar surfactants derived from renewable biomass, known for their biodegradability [3]. Specifically, we investigated the use of various glucosides for solubilizing terpenes (limonene, α -pinene, eucalyptol, p-cymene). Through optimized formulations, we achieved terpene solubility up to 25 wt% of the total mixture (Figure 1). Furthermore, controlled water content within the NADES system was found to not only influence fragrance solubility but also significantly impact the internal structure and viscoelastic properties of the final formulations (Figure 1). This tunable property holds promise for applications in cosmetics and topical drug delivery systems, such as creams.

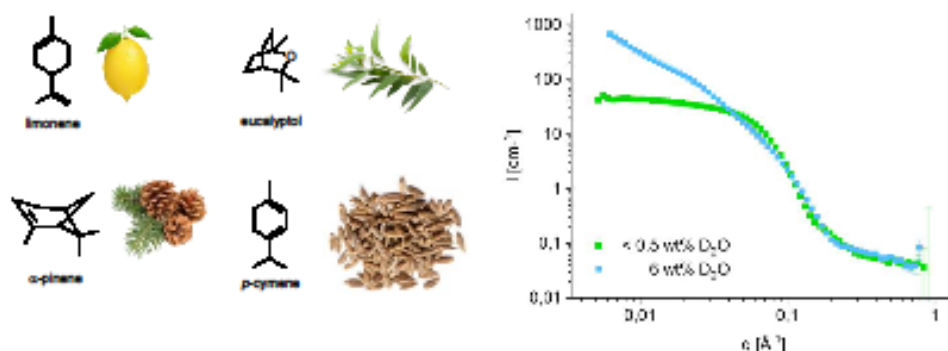


Figure 1. Left: Chemical structures of four terpenoids (limonene, α -pinene, eucalyptol and p-cymene) and their sources in nature (lemons, pines, eucalyptus, cumin). Right: SANS of eucalyptol solution (200 mM) in reline with different D₂O content (ISIS).

Acknowledgements: The authors acknowledge funding from BMBF, grant Number 05K19KT2.

References

- [1] M. Martins, L. Silva and O. Ferreira, *Journal of Molecular Liquids*, 2017, 241, 996-1002, 241.
- [2] E. L. Smith, A. P. Abbott, and K. S. Ryder, *Chemical Reviews*, 2014, 114 (21), 11060-11082.
- [3] Per M. Claesson, *Encyclopedia of Surface and Colloid Science*, 3rd Ed., 2015, Sugar Surfactants, 6917-6937, CRC Press, City, Country.

Peptide grafting into mesoporous silica for transport control, controlled release, and wound healing

Mohadeseh Bagherabadi¹, and Annette Andrieu-Brunsen¹

¹ *Technische Universität Darmstadt, Darmstadt, Germany*

Presenting author e-mail: Mohadeseh.bagherabadi@tu-darmstadt.de

Keywords: Short peptide, Mesoporous silica, BODIPY, Ion transport, Bio-functionalization, Wound healing

Porous silica, characterized by its large specific surface area and finely tuned nanoscale pore structures, presents an appealing platform for integrating peptides. This fusion results in hybrid materials termed peptide-nanomaterial conjugates, offering promising prospects for loading and releasing therapeutic agents in drug delivery and wound healing systems. Wound infections, particularly in burn injuries, pose a significant challenge due to the complexity of changing wound dressings and bacterial resistance. We investigate the design of peptide sequences in mesoporous silica and their effect on ion transport, facilitating subsequent release. Mesoporous silica coatings are synthesized via sol-gel chemistry and evaporation-induced self-assembly, achieving well-defined mesoporous structures. Mesoporous silica is functionalized utilizing BODIPY-N3 as a linker [1] which facilitates the visible light-triggered release. Peptides are attached to the BODIPY-N3 by grafting from and grafting onto approaches. The functionalization and ion transport were confirmed using ATR-IR, cyclic voltammetry, ellipsometry, and fluorescence analysis. It was observed that the peptide sequences affect the optical properties and fluorescence intensity of the coating as well as the ionic pore accessibility. We demonstrate that ion transport can be modulated by adjusting the sequence and charge of peptides within functional mesoporous films. The release of the peptide from the nanomaterial coating in wound dressing fabrics is expected to present an advancement in future wound treatment technologies.

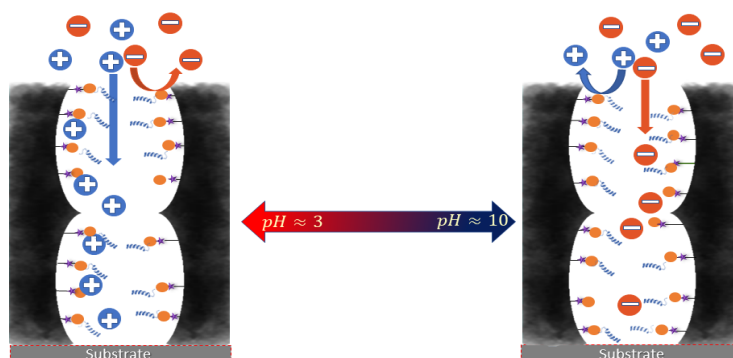


Figure 1. Schematic illustration of the synthesis of ultra-short peptides on mesoporous films and its effect on ion transport.

References

1. Bagherabadi, M. and A. Andrieu-Brunsen, *Ultrashort Peptide Grafting on Mesoporous Films and Its Impact on Ionic Mesopore Accessibility*. Langmuir, 2024.

Exploring Thermal-Responsive Structural Changes in Unilamellar Phospholipid Vesicles Induced by Interaction with Di-Rhamnolipids

Tim Julian Stank¹, Martin Bick¹ and Thomas Hellweg¹

¹ *Physical and Biophysical Chemistry, Universität Bielefeld*

Presenting author e-mail: tim.julian.sta@uni-bielefeld.de

Keywords: Di-rhamnolipids, DMPC, membrane interactions, SAXS, WAXS, UV-Vis Turbidity

Rhamnolipids are microbial biosurfactants with strong surface activity and remarkable emulsifying properties. They have gained greater attention and are considered one of the most important and promising biosurfactants in the cosmetics and pharmaceutical industries due to their fungicidal and antibacterial properties, low human toxicity and high biodegradability.^[1-4] In addition, they can be obtained in an environmentally friendly way through microbial production, e.g. by the bacterium *Pseudomonas aeruginosa*, using sugar or cooking oils as carbon sources.^[5]

Rhamnolipids belong to the group of glycolipids and can be classified as mono-rhamnolipids (RL; Rha-Cx-Cy) or di-rhamnolipids (dRL; Rha-Rha-Cx-Cy) based on the number of rhamnose molecules as the hydrophilic headgroup. Additionally, they possess one or two alkyl chains varying from C8 to C14 as hydrophobic tails.^[1-7]

The biological activity of rhamnolipids is attributed, among other factors, to their interaction with biological membranes. Previous studies have shown that depending on external parameters such as temperature and pH, rhamnolipids tend to self-assemble into various structures, including micelles, vesicles, bilayers, or stacked structures.^[2-4] Given their diverse potential applications, investigating the interaction of rhamnolipids with phospholipid membranes is of great interest.

In this study, we examined the interaction of a commercially available di-rhamnolipid product, containing a mixture of Rha-Rha-C10-C10 and Rha-Rha-C10-C8, with model membrane systems composed of 1,2-dimyristoyl-*sn*-glycero-3-phosphocholine (DMPC) under physiological pH conditions, while varying temperature and dRL concentration. We performed temperature-dependent UV-Vis turbidity measurements, as well as small-angle (SAXS) and wide-angle X-ray scattering (WAXS) measurements at dRL concentrations above the critical micelle concentration (CMC) revealing a highly complex phase behaviour. The results suggest structural transitions from vesicles at low temperatures and low dRL concentrations to first highly ordered formations occurring above the main phase transition temperature (T_m) of DMPC (23.4 °C). Upon further increase in temperature above 40 °C large aggregated structures were observed.

With increasing dRL concentration the diameter of the vesicles decreases. For high dRL concentrations and temperatures above 30 °C, larger monodisperse vesicles were found. WAXS measurements confirmed a decrease in the phase transition temperature of the phospholipid membrane by the introduction of dRL.

[1] L. R. Rodrigues, *Journal of colloid and interface science*, 2015, **449**, 304–316, <https://www.sciencedirect.com/science/article/pii/S0021979715000570>.

[2] N. Baccile, A. Poirier, J. Perez, P. Pernot, D. Hermida-Merino, P. Le Griel, C. C. Blesken, C. Müller, L. M. Blank and T. Tiso, *Langmuir: the ACS journal of surfaces and colloids*, 2023, **39**, 9273–9289.

[3] F. J. Aranda, M. J. Espuny, A. Marqués, J. A. Teruel, A. Manresa and A. Ortiz, *Langmuir*, 2007, **23**, 2700–2705.

[4] T. Hellweg, T. Sottmann and J. Oberdisse, *Front. Soft. Matter*, 2023, **2**.

[5] T. A. A. Moussa, M. S. Mohamed and N. Samak, *Braz. J. Chem. Eng.*, 2014, **31**, 867–880.

[6] D. Gogoi, P. Bhagowati, P. Gogoi, N. K. Bordoloi, A. Rafay, S. K. Dolui and A. K. Mukherjee, *RSC Adv.*, 2016, **6**, 70669–70681.

[7] M. Nie, X. Yin, C. Ren, Y. Wang, F. Xu and Q. Shen, *Biotechnology Advances*, 2010, **28**, 635–643, <https://www.sciencedirect.com/science/article/pii/S0734975010000649>.

Janus Droplet Liquid Sensing Platform with Automated Real-Time Morphology Monitoring

Yuzi Hong¹, Bradley D. Frank¹ and Lukas Zeininger¹

¹Department of Colloid Chemistry, Max Planck Institute of Colloids and Interfaces, Potsdam, Germany

Presenting author e-mail: Yuzi.Hong@mpikg.mpg.de

Keywords: complex colloids, emulsions, surfactants, sensors, high-throughput device

Liquid sensing platforms are crucial for environmental protection, product quality assurance, and scientific innovation. Traditional methods for detecting aqueous pollutants and ensuring water quality, such as HPLC and GC-MS, are often time-consuming, expensive, and laboratory-based. As an alternative, liquid-liquid chemo- and biosensors offer a promising on-site pre-monitoring solution, resembling natural recognition environments and complementing existing techniques.

Oil-in-water emulsion droplets are useful for environmental monitoring due to the ease of preparation in diverse settings. Their hydrophobic-hydrophilic interfaces facilitate reactions between synthetic surfactants, which are often organo-soluble, and analytes in aqueous environments. These droplets are stabilized by surfactants and exist in dynamic, thermodynamic out-of-equilibrium states, with molecules continually exchanging between the droplets and surroundings. Interface-selective sensitization allows for programmed up and down-regulating capabilities. Dynamic interfacial host-guest complexation can trigger morphological changes that resemble cell surface environments. Emulsion droplets act as messenger colloids, visualizing and reporting chemical changes with exceptional sensitivity, and detecting levels as low as femtomolar [1].

Previous studies succeeded in analyzing individual droplet shapes but were limited in high-throughput and multiplexing capabilities. We developed a rapid analytical tool for multiplexed high-throughput screening, parallel prescreening, or semi-quantitative diagnostics, utilizing Janus emulsions containing hydrocarbon and fluorocarbon oils stabilized by two surfactants. An inert surfactant to maintain stability during stimulation and a stimuli-responsive surfactant that is sensitive to specific functional groups of analytes. These droplets have shown significant potential as liquid sensing materials, detecting various analytes including small molecules, metal ions, viruses, and bacteria [2]. The droplet morphologies were analyzed using customized sideview microscopy, coupled with a real-time droplet morphology monitoring system, following the addition of analytes to the droplet-containing environments. Key parameters for characterizing morphology, other than interfacial tensions, are contact angles, volume ratios, surface area ratios, and snowman angles. The images were processed using MATLAB algorithms to extract essential parameters and generate calibration curves for further analysis. The results demonstrate that the sensing machine can accurately differentiate between analytes in a short period of time.

Automated Complex Janus droplet-based sensing devices offer great potential for distinguishing between different aqueous samples. They have leading advantages such as low cost, short response times, and high accuracy, making them ideal for rapid monitoring of environmental pollution, diagnostic markers, and water quality.

References

- [1] Zeininger, L., *Responsive Janus droplets as modular sensory layers for the optical detection of bacteria*. *Anal Bioanal Chem*, 2023. **415**(21): p. 5205-5219.
- [2] Barua, B., et al., *Multiplexed and continuous microfluidic sensors using dynamic complex droplets*. *Soft Matter*, 2023. **19**(10): p. 1930-1940.

Interfacial Properties and Phase Behavior of Mannosylerythritol Lipids and Mixtures with Anionic Surfactants

Moritz Stanek,¹ Janine Birnbach,² Peter Schmiedel,² and Guillaume Delaittre¹

¹University of Wuppertal, Organic Functional Molecules, Gaußstraße 20, 42119 Wuppertal, Germany

²Henkel AG & Co. KGaA, Henkelstraße 67, 40589 Düsseldorf, Germany

Presenting author e-mail: moritz.stanek@uni-wuppertal.de

Keywords: biosurfactants, microemulsion, interfacial tension, adsorption

In order to reduce greenhouse gas emissions, the substitution of fossil-based resources is of great importance. One class of renewable resources is that of biosurfactants, such as mannosylerythritol lipids (MEL). Biosurfactants are microbial products with low toxicity and biodegradability.[1] However, the replacement of conventional surfactants by biosurfactants is complex.[2] Hence, systems containing biosurfactants require fundamental physico-chemical investigations and synergistic combinations with other sustainable surfactants must be identified.

In the present study, the equilibrium and non-equilibrium physico-chemical properties of two different structures of MEL were investigated (see Figure 1, variants 1 and 2). It was found that the phase boundaries of the microemulsion of dodecyl tetraethylene glycol ether (C₁₂E₄) shift towards lower temperatures upon addition of the more hydrophobic structure, variant 1. Furthermore, low interfacial tensions for this MEL structure were found at equilibrium. The more hydrophilic variant 2 on the other hand shifts the phase boundaries of the microemulsion of C₁₂E₄ to higher temperatures. In addition, fast adsorption on the surface/oil-water-interface was observed for this MEL variant. To find synergistic combinations, both lipids were combined with either sodium dodecyl sulfate (SDS) or sodium dihexyl sulfosuccinate (SDHS). When the MEL variant 1 was combined with SDHS, lower interfacial tension at equilibrium were observed. In addition, variant 2 showed a faster adsorption velocity when combined with one of the anionic surfactants.

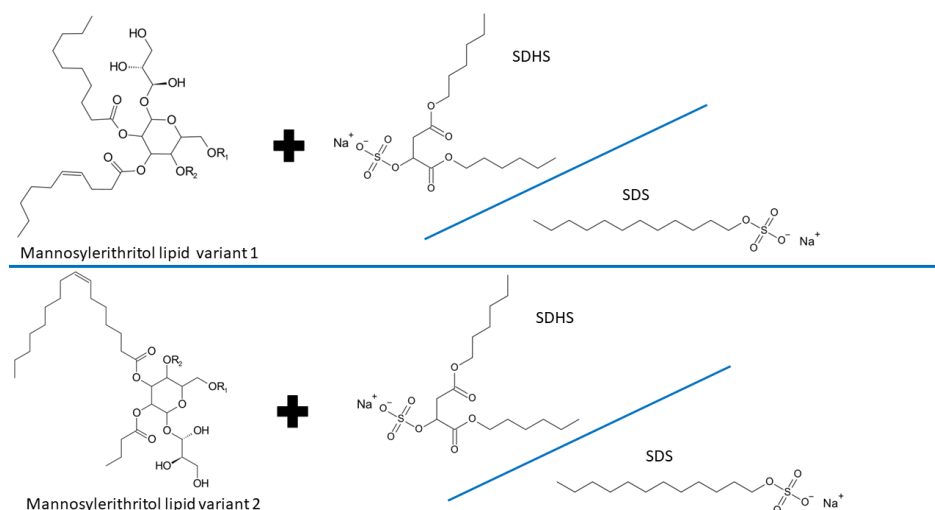


Figure 1. Structure of the different surfactants used.

References

- [1] I. O. Olasanmi, R. W. Thring, *Sustainability*, 2018, 10, 4817.
- [2] J. Birnbach, P. Schmiedel, M. Karg, *Curr. Opin. Colloid Interface Sci.*, 2023, 68, 101765.

Droplet Springs: Structuring liquids with programmable transience via interfacial jamming of pH-responsive block copolymers

Semira Bener¹, Lukas Zeininger¹

¹ *Department of Colloid Chemistry, Max Planck Institute of Colloids and Interfaces, Am Muehlenberg 1, 14476 Potsdam*

Presenting author e-mail: Semira.Bener@mpikg.mpg.de

Keywords: complex emulsions, Janus droplets, pH-responsive surfactants, responsive soft matter

Complex emulsions with tunable morphologies offer significant potential in various applications. This study investigates the manipulation of droplet geometries, transitioning between encapsulated and snowman configurations, through the modulation of interfacial tensions using hydrocarbon and fluorinated surfactants, alongside a pH-sensitive surfactant.

The fabrication process makes use of the temperature-dependent miscibility of hydrocarbon (HC) and fluorocarbon (FC) liquids, [1] with proportional replacement of the fluorocarbon component to elevate the upper critical solution temperature (UCST) towards a volatile co-solvent. Emulsification of the modified combination results in complex droplets elongated in the vertical direction, exhibiting snowman-like shapes.

Controlled confinement of pH-sensitive amphiphilic block copolymeric surfactant at interfaces was employed to dynamically lock droplet morphologies. [2] Experimental results demonstrate that gradually replacing FC surfactants with HC surfactants results in encapsulated droplet morphologies. At elevated pH levels, the block copolymer loaded in the hydrocarbon phase irreversibly adsorbs to the interfaces, thereby preventing dynamic morphological transitions upon returning to FC surfactant environments. However, upon decreasing the pH of the continuous phase enables partitioning of the co-polymers inside the droplets, allowing the droplet to transition from encapsulated to snowman-like morphologies, and thus to dramatically vary the droplets' aspect ratio.

These findings hold promise for applications in power-amplified synthetic systems, and shape-changing soft robotics inspired by biological mechanisms.

References

- [1] J. Guzowski, P. M. Korczyk, S. Jakiela, P. Garstecki, *Soft Matter*, 2012, 8, 7269.
- [2] B. Barua, T. J. Durkin, I. M. Beeley, A. Gadh and S. Savagatrup, *Soft Matter*, 2023, 19, 1930.

Structure of Microgels in Dense Monolayers

Simon Schog¹, M. Friederike Schulte¹, Steffen Bochenek¹ and Walter Richtering¹

¹ RWTH Aachen University, Institute of Physical Chemistry, Landoltweg 2, 52074 Aachen

Presenting author e-mail: schog@pc.rwth-aachen.de

Keywords: microgels, Langmuir-Blodgett depositions, atomic force microscopy, force spectroscopy

Microgels are three-dimensionally crosslinked polymer network that can swell in a good solvent (usually water). They can adapt their size and internal structure in response to environmental stimuli, such as temperature, pH, or ionic strength. Microgels are highly interfacially active and possess a rich phase behavior due to their inhomogeneous soft structure. They can be used, e.g., as emulsion stabilizers or as surface coatings [1].

In this study, microgel monolayers were prepared via Langmuir-Blodgett depositions at different interfacial concentrations [2]. The monolayers were investigated ex-situ using atomic force microscopy / force spectroscopy [3] to investigate the structure and topography of the monolayers as well as the internal structure of microgels within the monolayers at the solid-liquid interface at different temperatures. Force-Distance curves and their features were analyzed using custom written MATLAB codes to extract the contact stiffness of the microgels which is proportional to the polymer density within the microgels.

The results of our measurements show that the confinement of microgels within monolayers has a profound effect on the internal structure of microgels. Single microgels possess an inhomogeneous internal structure with a stiffer center and less stiff periphery. The compression of the microgels within dense monolayers has little impact on the lateral dimensions of the microgels at the solid-liquid interface and only a slight increase in height can be detected upon compression. However, the microgels become noticeably stiffer in their center at high compressions, indicating an increase in polymer density.

Acknowledgements: The authors acknowledge funding from the Deutsche Forschungsgemeinschaft (DFG) for financial support within project B8 of the Sonderforschungsbereich SFB 985 “Functional Microgels and Microgel Systems”.

References

- [1] F. Plamper, W. Richtering, *Accounts of Chemical Research*, 2017, 50, 131.
- [2] S. Bochenek, A. Scotti, W. Ogieglo, M. A. Fernández-Rodríguez, M. F. Schulte, R. A. Gumerov, N. V. Bushuev, I. I. Potemkin, M. Wessling, L. Isa, W. Richtering, *Langmuir*, 2019, 23, 51, 16780.
- [3] M. F. Schulte, S. Bochenek, M. Brugnoli, A. Scotti, A. Mourran, W. Richtering, *Angew. Chem. Int. Ed.*, 2020, 133, 5, 2310.

In-situ monitoring of core-shell microgel monolayers

Julian Ringling¹, Keumkyung Kuk¹, Vahan Abgarjan¹ and Matthias Karg¹

¹ *Physikalische Chemie I, Heinrich-Heine Universität, 40225 Düsseldorf, Germany*

Presenting author e-mail: julian.ringling@hhu.de

Keywords: Core-shell microgels, colloidal self-assembly, microgel-substrate interaction,

Hard-core soft-shell microgels are fascinating colloids that hold promise for applications in various fields such as emulsion stabilization and as valuable model systems for elucidating crystallization and melting phenomena [1]. These surface-active microgels disperse across flat fluid interfaces, where they self-assemble into two-dimensional monolayers with a distinct lack of direct core-to-core contact, a consequence of shell-shell repulsion forces. Manipulating these monolayers involves compressing the soft, deformable shell to exert control over inter-particle distances [2]. Such monolayers are commonly explored by transferring them onto a substrate using a Langmuir trough, followed by employing microscopy techniques such as atomic force microscopy or scanning electron microscopy to analyse the arrangement of microgels [2].

In our prior research, we demonstrated that large microgels at the air/water interface do not undergo an isostructural phase transition [3], contrary to what has been described in literature [2, 3]. It seems that the proposed isostructural phase transition can be attributed to a drying artifact. This highlights the importance of utilizing *in-situ* methods to analyse the microgel arrangement directly at the air/water interface. By utilizing the high contrast of the inorganic core and the large size of the PNIPAM shell, we can resolve individual microgels using light microscopy or small angle light scattering to study ensemble properties [3].

Here we present findings from observing microgel monolayers at the air/water interface and throughout the drying process on a substrate, with particular focus on the alterations in microgel arrangement to variations in substrate surface chemistry and microgel crosslinking density.



Figure 1. Microgel monolayer drying on a hydrophobic substrate. The monolayer is drying towards the left side, where the meniscus is visible. Scale bar = 10 μ m.

References

- [1] Z. Dai, T. Ngai, *Journal of Polymer Science*, 2013, 51, 2995 - 3003
- [2] J. S. J. Tang, R.S. Bader, E. S. A. Goerlitzer, J. F. Wendisch, G. R. Bourret, M. Rey, N. Vogel, *ACS Omega*, 2018, 3 12089 – 12098
- [3] K. Kuk, V. Abgarjan, L. Gregel, Y. Zhou, V. Carrasco Fadanelli, I. Buttinoni, M. Karg, *Soft Matter*, 2023, 19, 175 - 188