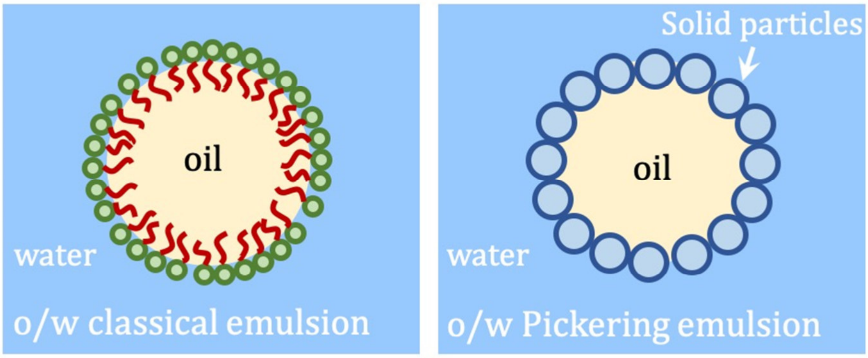
How optical stability analysis can help to study Pickering Emulsions.

Emulsion stability for biomedical applications is a tricky issue still to solve. Normally a good surfactant can keep an oil-in-water emulsion stable for a long time but surfactants can be harmful when applied in the human body and in general the number of approved substances in pharma production is very limited.

Pickering emulsions got to be a promising alternative for biomedical applications because of a different stabilization mechanism that doesn´t require any other external substances in the final product.

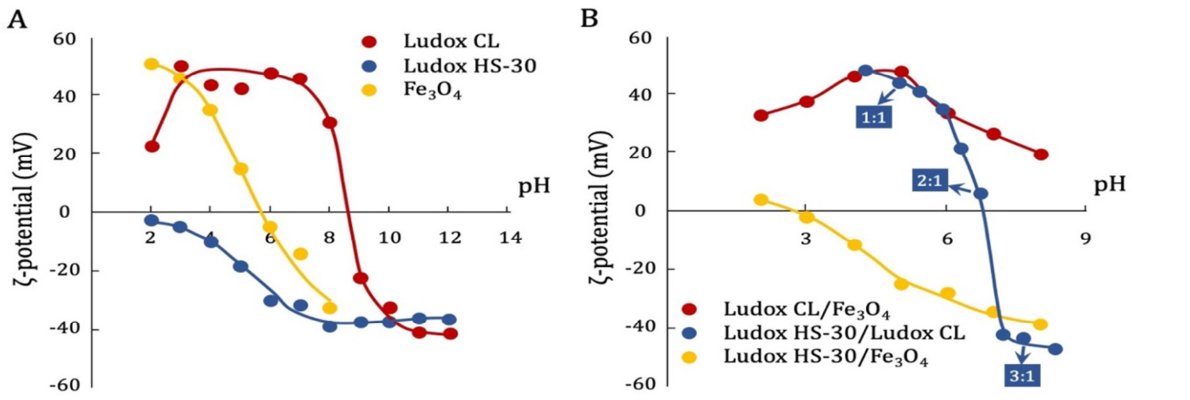
Pickering emulsions are stabilized by solid particles which arrange at the interface between water and an oil phases (o/w) (**Picture 1**). This phenomenon has been intensively studied amongst others in the field of biomedical applications like colloidal micro/nano capsules as the transport possibility for pharmaceutical compounds to the right location in the human body. Depending on the pH-value of the ambience Pickering emulsions gets decomposed releasing the encapsulated active medicine in the desired location of the digestion tract.



Picture 1: *Schematic illustration of a classical emulsion and Pickering emulsion.*

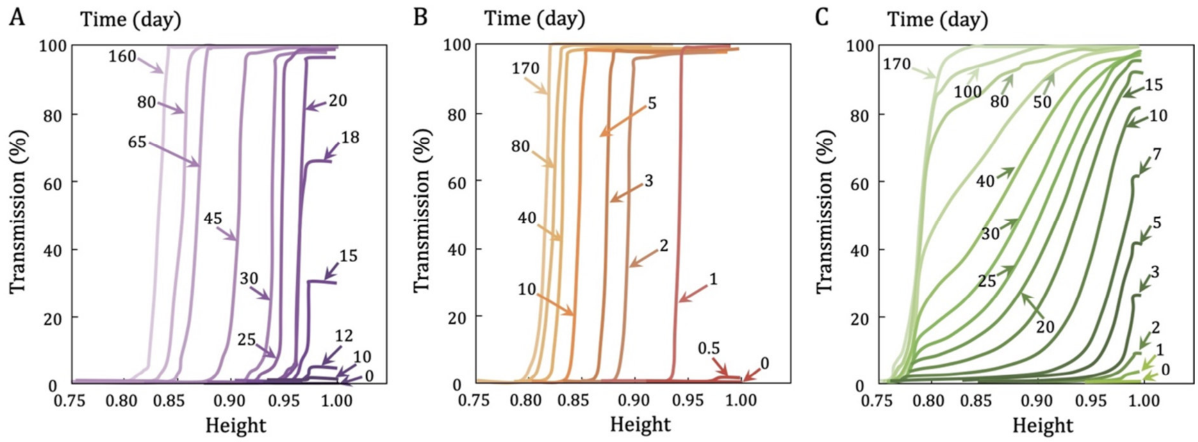
Recently, Koroleva et al. have proposed to stabilize emulsions with mixed oppositely charged particles (SiO_2 and Fe_3O_4 nanoparticles). The introduction of these magnetite particles can lead to magnet-induced particle association, enhancing the strength of droplet networks responsible for preventing coalescence and keeping the long-term physical stability of the emulsions.

In this work, negatively charged silica nanoparticles Ludox HS-30, positively charged alumina-coated silica nanoparticles Ludox CL and Fe_3O_4 nanoparticles were used to study the mechanism of stabilization. The ζ-potential is a key parameter to understand the stability of particles caused by the electrical charge on the surface of the particles. It can well be imagined that particles with the same surface charge will repel each other while particles with opposite charges attract each other. As instability often arises from agglomeration processes, the authors first measured the ζ-potential in dependence of the pH value. **Picture 2** shows that the pH of the aqueous phase played a role in the ζ-potential of the nanoparticles (Ludox HS-30, Ludox CL and Fe_3O_4) and nanoparticle mixtures (Ludox HS-30/Fe_3O_4, Ludox CL/Fe_3O_4 and Ludox HS-30/Ludox CL). This leads to the conclusion that also the stability of these emulsions will strongly depend on the pH-value which was studied next with Ludox HS-30/Ludox CL at different ratios as the model system.



Picture 2: *The ζ-potential of the nanoparticles (A) and nanoparticle heteroaggregates (B) as a function of the pH of the aqueous phase in suspension.*

The stability of aqueous Ludox HS-30/Ludox CL suspensions was analyzed with the optical stability analysis system MS 20 from DataPhysics by measuring the transmitted light intensity of the suspension inside a test vial at various heights (**Picture 3**).



Picture 3: *The transmitted light intensity in the suspensions of SiO_2 nanoparticles. Mass ratios of Ludox HS-30 to Ludox CL nanoparticles were 1: 1 (A), 2: 1 (B), 3: 1 (C).*

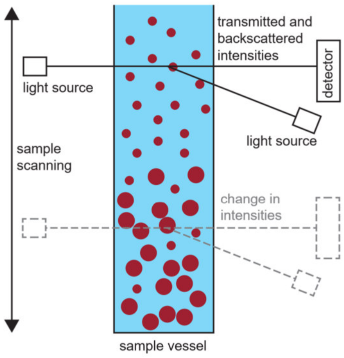
A. The ζ-potential of Ludox HS-30/Ludox CL-1:1 was +45 mV (**Picture 2B**) leading to a strong particle repulsion and thus to repulsion of the oil droplets in the Pickering emulsion. **Picture 3A** shows the aggregation formed slowly and the gel-like network formed in 20 days;
B. The ζ-potential of Ludox HS-30/Ludox CL-2:1 was close to 0 (**Picture 2B**) leading to almost no repulsion and thus in **Picture 3B** the formation of nanoparticle aggregation and a gel-like network can be seen already after 1 day from the vertical curve.

C. The ζ-potential of Ludox HS-30/Ludox CL-3:1 was -44 mV (**Picture2**) and **Picture 3C** shows as slow change like in **Picture 3A.** However, the sedimentation behavior significantly differs from the other mixture which was explained by the formation of large heteroaggregates which slowly precipitate.

The Stability Analysis System MS 20

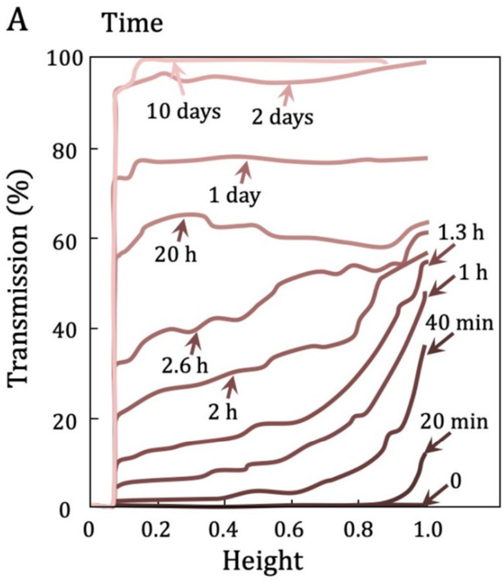
The MultiScan MS 20 is a measuring device for the automatic optical stability and aging analysis of a variety of multi-phase dispersions, in particular suspensions and emulsions, and the comprehensive characterization of **time- and temperature-dependent destabilization mechanisms**.

The **transmission** and **backscattering intensity** is scanned and recorded position dependently this allows to detect processes such as **agglomeration, coalescence, sedimentation, creaming and the clouding** which is reported in the current article.



Due to its modular design the MS 20 can be operated with up to six scan towers. The scan towers are independently controllable, which allows to perform **several measurements simultaneously under individual conditions**.

Furthermore, the authors also studied the pH dependence of the stability. Emulsions stabilized with Ludox HS-30 and Fe_3O_4 nanoparticles were stable at pH 2-6, because these two nanoparticles had the opposite or close to zero charges at this pH range. Likewise, emulsions stabilized with Ludox CL and Fe_3O_4 nanoparticles were stable at pH 6-8. **Picture 4** illustrated the stability for the mixture of Ludox HS-30/Fe_3O_4 nanoparticles at pH 2. Due to the attractive electrostatic interactions, Ludox HS-30/Fe_3O_4 nanoparticles suspensions aggregated rapidly, then grew and finally precipitated at the bottom of the vessel.



Picture 4: *The transmitted light intensity in suspensions of Ludox HS-30 and Fe_3O_4 nanoparticles at pH 2*

Overall, the authors clarified that emulsion stabilization could be tuned by the mass ratio of Ludox HS-30 and Ludox CL nanoparticles in emulsions. It could furthermore be shown that the pH value plays a major role in preventing an agglomeration causing stability issues. Knowing these key parameters and their effects can be a valuable guideline for utilizing Pickering emulsions in biologic environments.

The optical stability analysis system MultiScan MS 20 (DataPhysics Instruments GmbH, Germany) was used in this research.

For more information, please refer to the following article:

Emulsions stabilized with mixed SiO_2 and Fe_3O_4 nanoparticles: mechanisms of stabilization and long-term stability; M. Koroleva, D. Bidanov and E. Yurtov; *Phys.Chem.Chem.Phys.,* ***2019****, 21, 1536*; DOI: 10.1039/c8cp05292a