# Emulsions Stabilized by Nanoparticles: Microfluidics and Traditional Production

M. J .B Moura, M. S. Carvalho, M. F. G. Huila, A. Parussulo, K. Araki, J. O. Fossum

mariamoura@puc-rio.br; msc@puc-rio.br; manfergo.chemistry@gmail.com; andrearaujo161@gmail.com; koiaraki@iq.usp.br; jon.fossum@ntnu.no

**Abstract:** *Emulsions are essential to a wide range of industries, such as food, pharmaceutical, and petrochemical. Here we present a study of the stabilization of oil in water emulsion with modified titanium dioxide nanoparticles (TiO2-HAc). We tested different nanoparticle concentrations to produce stable emulsions via microfluidics and large scale methods. We studied the effect of the nanoparticles on the fluids' interface by measuring interfacial tension and viscoelasticity. We also obtained images of the nanoparticle network on the droplets surfaces using confocal Raman microscopy. The produced emulsions have droplet sizes of 40 to 1000* μm *and are stable for months. Our final goals are to produce emulsions with specific mechanical properties, and to use these emulsions to control water mobility through heterogeneous porous media.*

**Key-Words***: Pickering emulsions ; microfluidics ; interfacial tension ; porous media*

**Introduction:** A Pickering emulsion is an emulsion that is stabilized not by surfactants, but by particles that adsorb onto the interface between the two fluids. Our interest in Pickering emulsions is to produce droplets with specific mechanical properties to inject in porous media in order to control water mobility. These emulsions, with controlled properties, can be achieved by varying the droplet sizes and particle concentration. Here we present two methods for producing Pickering emulsions of TiO2-HAc: traditional methods using an ULTRA-TURRAX mixer, and microfluidics. With microfluidics it is possible to produce droplets in a controlled fashion, but on small scale. On the other hand, with traditional methods it is possible to produce large volumes, but the emulsions are more polydisperse. In order to develop the best emulsion for our purpose we tested both methods.

**Experimental:** We produced emulsions of oil in water stabilized by TiO2-HAc nanoparticles. The oil phase is filtered Drakeol 7 and the aqueous phase is a suspension of nanoparticle with or without salt (NaCl 3% w/w). Dispersions of different nanoparticle concentrations were tested.

Via microfluidics the emulsions are produced using a glass microcapillary device [1], shown in Fig. 1. The fluids are injected independently using syringe pumps. The salt helps to stabilize the emulsion by forming aggregates and decreasing the affinity of the particles for water. For this reason the salt is injected separately, to prevent the particles from aggregating and precipitating before they reach the droplets´ interface. A microscope and a high-speed camera are used to monitor and capture images of the production.

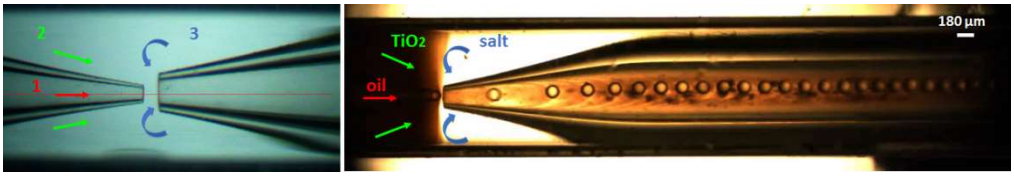


Figure 1: Emulsion production with microfluidic device.

In the production via traditional methods all fluids are mixed together using an ULTRA-TURRAX according to the concentrations shown in Table 1.

Using the pendant drop method with a Tensiometer (Teclis instruments) we also performed steady-state and oscillatory tests on a drop of TiO2-HAc dispersion in oil to obtain the interfacial tension and viscoelastic modulus.

**Results and discussion:** The emulsions produced via traditional methods are polydisperse, with a variation in size of approximately 20%, see Table 1. These emulsions have been observed to be stable over months.

| ***Sample*** | ***1*** | ***2*** | ***3*** |
|---|---|---|---|
| Droplet diameter (µm) | 40.6 ±7.7 | 89.0±14.8 | 61.9±11.2 |
| Oil volume (ml) | 10 | 20 | 10 |
| Water volume (ml) | 70 | 100 | 70 |
| TiO2 (% w/w) | 0.23 | 0.16 | 0.15 |

Table 1: Emulsion via traditional method – concentrations and results.

In microfluidics we were able to fabricate droplets using TiO2 dispersion (0.46% w/w) at 9 ml/hr, NaCl (3% w/w) at 9 ml/hr, and Drakeol at 1 ml/hr (see Fig. 1). The produced droplets have diameters of approximately 200 µm, but they coalesce, and end up with ~1000 µm. For dispersions with a higher particle concentration (1.84% w/w) and injection rates of 30 ml/hr for the TiO2 and the salt and 0.01ml/hr for the oil we are able to produce droplets of the order of 100 µm, but some coalescence is still observed and we end up with droplets of 100 to 500 µm.

We observed that it easier to stabilize the emulsion via TURRAX than via microfluidics, probably because the turbulence helps the particles to reach the interface, while in microfluidics we depend on laminar flow and diffusion to spread the particles. To develop a better understanding of the time scale and particle concentration required to stabilize these emulsions we performed studies of the effect of the nanoparticles on the fluids interface by measuring interfacial tension and viscoelasticity. The tests show that the interfacial tension decreases with an increase in particle concentration, similar to the effect of surfactants (see Fig. 2). Also the elastic modulus increases with an increase in particle concentration. No significant change is observed for the viscous modulus. However the elasticity is weak and it takes a long period of time and a large concentration of particles to stabilize the interface TiO2-oil only through diffusion. Fig. 2 shows that the aggregation of the particles on the interface is non-uniform. We are currently performing experiments with salt to test if that improves the TiO2-HAc film mechanical properties.

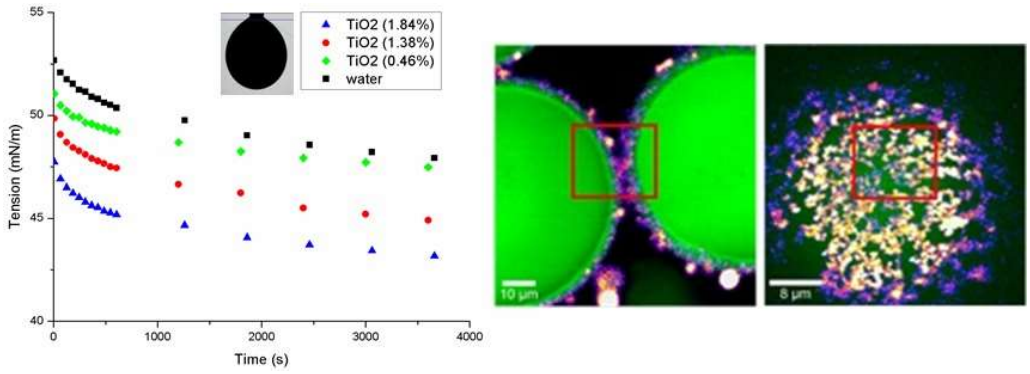


Figure 2: On the left: Interfacial tension of TiO2 drop in oil, for different particle concentrations. On the right: Confocal Raman image of emulsion produced via traditional method: Oil droplet (in green) with TiO2 "tentacles" (in purple) on the surface. The nanoparticles constitute a non-uniform coverage of the droplets surfaces of 2 to 4 µm in thickness.

**Conclusion:** We produced emulsions of oil in water stabilized by TiO2-HAc nanoparticles via microfluidics and traditional methods. The emulsions have droplet sizes of 40 to 1000 µm and are stable for months. At this point, emulsions via traditional methods can be stabilized with lower particle concentrations and less coalescence than via microfluidics. Our next step is perform injections of the produced emulsions in heterogeneous porous media to study water mobility control.

**References and acknowledgements:**

Refererences: [1] A. S. Utada, E. Lorenceau, D. R. Link, P. D. Kaplan, H. A. Stone, D. A. Weitz, Science, **2005,** 308, 537.

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