

# Monitoring Emulsions Morphology Under Shear via Simultaneous Rheometry and In-situ FT-IR Spectroscopy

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## Overview

**Purpose:** Investigation of the dynamics of molecular organization of emulsions with submicron droplets under shear.

**Methods:** Simultaneous rheometry and in-situ FT-IR spectroscopy utilizing the Rheonaut module.

**Results:** Provides insight into molecular organization and dynamics under deformational flow.

## Introduction

Emulsions are of wide interest in the food, pharmaceutical, healthcare and cosmetic industries. They typically consist of at least two liquid phases, surfactant agents and stabilizers. Emulsions exhibit complex rheology, making it difficult to understand flow phenomena on a microscopic level.

A common technique utilized to analyze emulsions under shear deformation is light microscopy. However, emulsions showing droplet distributions with droplets on the sub-micron scale cannot be visualized using light microscopy because of given resolution constraints. Other limiting factors of light microscopy arise when the concentration of droplets with equal size is high or the refractive indices of the two phases are too similar.

In such cases, the Thermo Scientific HAAKE MARS rheometer equipped with the Rheonaut module and a FT-IR spectrometer provides simultaneous rheometry and in-situ FT-IR spectroscopy under shear deformation and offers a versatile tool for efficient and comprehensive emulsion research and stability testing. Simultaneous rheometry and FT-IR spectroscopy proves to be a useful tool in understanding the microscopic state of droplets in concentrated emulsions.

In this contribution, we want to present some results on the dynamics of molecular organization of an emulsion under shear.

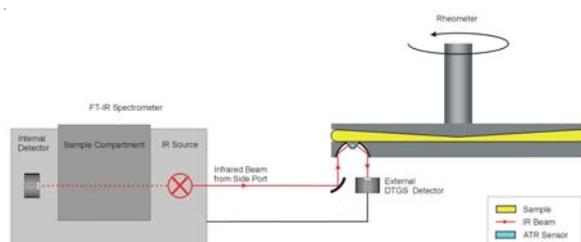


Fig. 1: Schematic diagram of coupling an FTIR spectrometer to the HAAKE MARS rheometer.

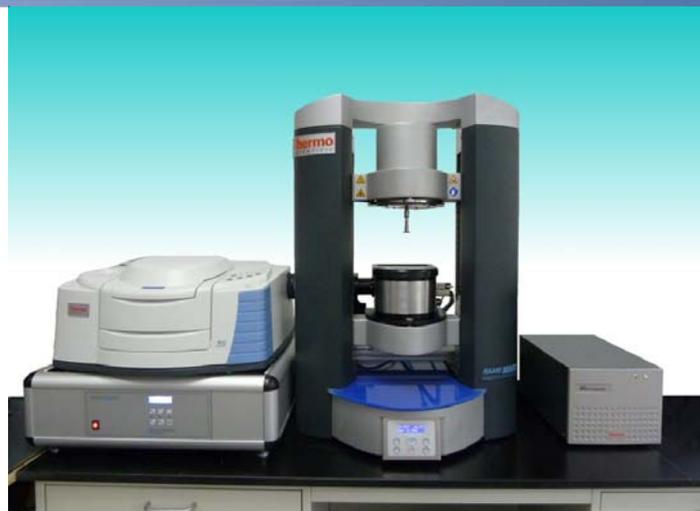


Fig. 2: HAAKE MARS rheometer with Rheonaut module and NICOLET iS10 FT-IR spectrometer.

## Materials

For this study, as model substances, three commercially available hand cream emulsions with high volume fractions of oil in water containing submicron droplets were supplied by a manufacturer of cosmetics. The samples varied with respect to their hydrocarbon composition only. No further sample preparation was required.

## Methods

The patented Rheonaut module couples a standard FT-IR spectrometer with side port (here: Thermo Scientific NICOLET iS10) to the Thermo Scientific HAAKE MARS rheometer.

The lower plate of the rheometer is temperature controlled (Peltier or electrical) and features a monolithic diamond element that serves as the ATR (attenuated total reflection) sensor, offering a single internal reflection. Compared to standard infrared transmission spectroscopy or specular reflection spectroscopy techniques, the sample thickness can thus be adjusted to the rheological needs and is independent from the infrared spectroscopy requirements.

The operation is managed by the HAAKE RheoWin software providing full control over temperature settings, horizontal positioning of the lower plate, and the communication with the FT-IR spectrometer software for synchronous data acquisition.

Steady shear flow experiments were carried out using a cone/plate measuring geometry with 20 mm diameter and a cone angle of  $2^\circ$ . Gap setting was 0.1 mm. All samples were tested in CR (controlled shear rate) mode from  $0.5$  up to  $500 \text{ s}^{-1}$ . The temperature was set to  $25.0 \pm 0.1 \text{ }^\circ\text{C}$ . The infrared spectral range was  $400 \text{ cm}^{-1}$  to  $4000 \text{ cm}^{-1}$  with a spectral resolution of  $4 \text{ cm}^{-1}$ . Each spectrum consists of 8 co-added scans. A complete data set was produced for each sample, consisting of 18 rheological data points and 18 related (simultaneously collected) FT-IR spectra.

## Results

Figure 3 displays the dynamic shear viscosity plotted against shear rate for the three samples #1, #2, and #3. As typical for highly concentrated emulsions, the materials show a decreasing viscosity with increasing shear rate (shear thinning or pseudoplastic).

A closer look, however, reveals a step-like shear thinning behavior as can be seen in the right graphs of figure 3 which display the viscosity plotted double-logarithmically against shear stress.

Such a viscosity behavior has been investigated amongst others by Saiki et al. [1]. Based on detailed rheological experiments, the proposed figurative model is a droplet distribution profile which changes with the applied stress. Whereas at very low shear the droplets are distributed homogeneously, ambiguous layers (or clusters) of droplets

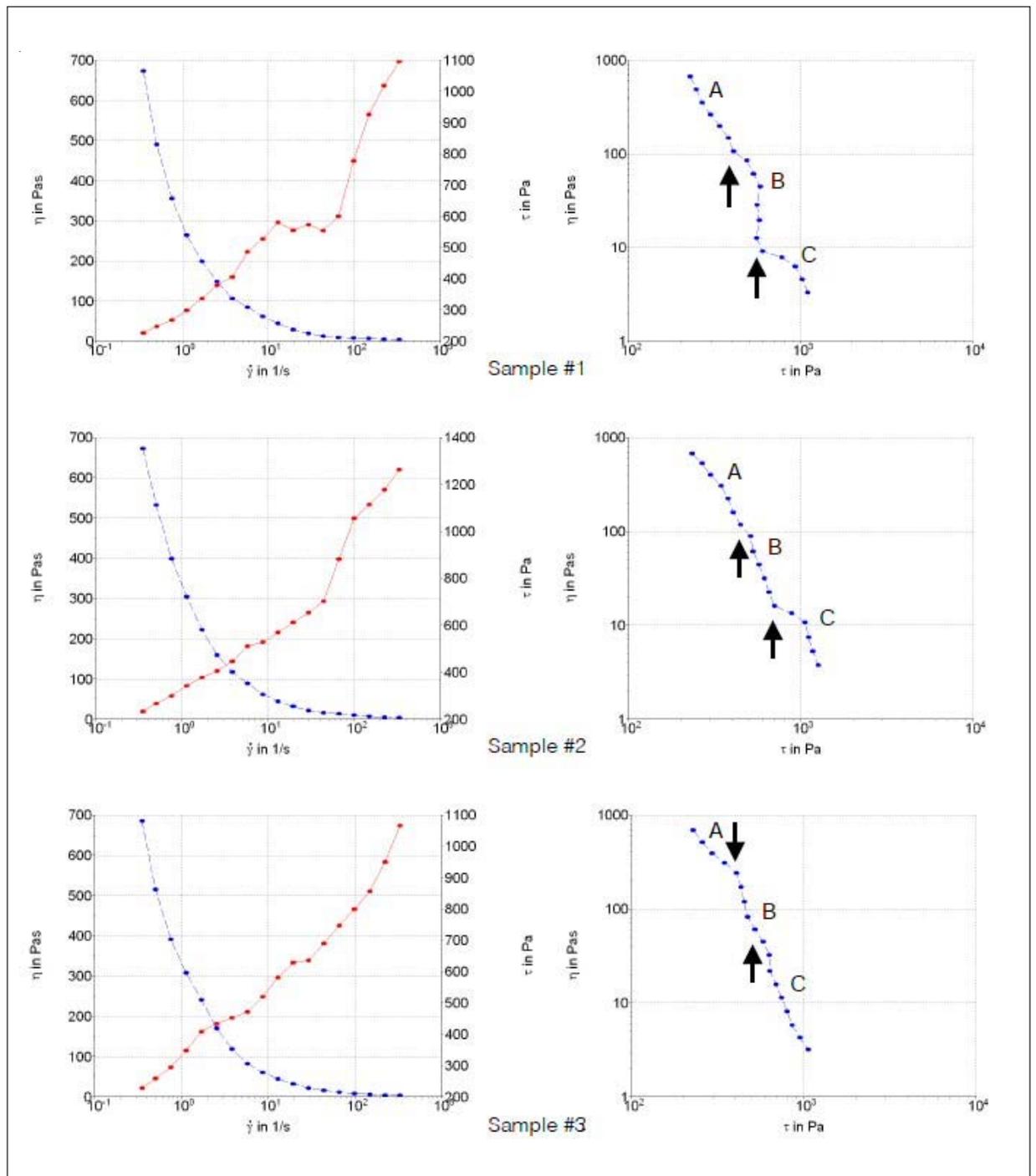


Fig. 3: Left column: Viscosity  $\eta$  (blue graph) and stress  $\tau$  (red graph) plotted against shear rate. Right column: Viscosity  $\eta$  (log scale) plotted against stress  $\tau$ .

are formed at moderate shear causing slight segregation in droplet population and at higher shear discrete layers are formed. Another approach [2] proposes a figurative model showing a droplet deformation and stretching by the applied shear, leading to droplet rupturing and recombination through coalescence at higher shear stresses.

Simultaneously applied FT-IR spectroscopy enables a more sophisticated molecular insight and deeper understanding. Figure 4 displays a typical FT-IR sample spectrum. The broad absorption band at  $3354\text{ cm}^{-1}$  relates to the aqueous phase of the sample whereas the band at  $2922\text{ cm}^{-1}$  relates to the organic phase.

The sample changes with shear get easily traceable by calculating the absorption ratio ( $3354\text{ cm}^{-1}/2922\text{ cm}^{-1}$ ) from each spectrum and plotting the results against the experimental procedure (figure 5).

The change of the infrared absorption ratios in figure 5 reveals a concentration gradient within the samples. Close to the ATR sensor are sample layers at which the organic phase is enriched in relation to the aqueous phase.

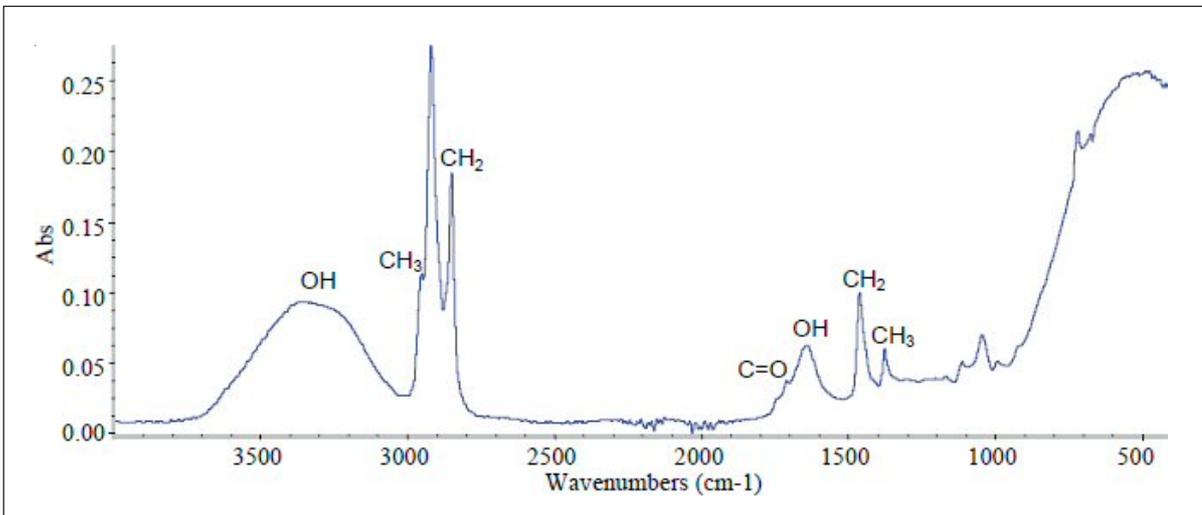


Fig. 4: A typical FT-IR absorbance spectrum with band assignments of the investigated samples.

As the experiment goes on, the enrichments dissolve again. Because the ATR sensor area dimensions are several orders of magnitude larger than the submicron droplets of the organic phase, neither droplet deformation and stretching nor coalescence is an object since they do not evoke a concentration gradient within a sample.

The shear thinning behavior of the investigated emulsion samples is initially controlled by perturbation and breakdown of complex droplet structures which lead to the formation of droplet layers causing flatter shear viscosity curve regions. With further increasing shear rates, however, a self-healing process is observed. The droplet structure is rearranged and hence the layers are dissolved, as the FT-IR spectra show.

## Conclusion

Rheometry and FT-IR spectroscopy have been applied simultaneously on model emulsions (3 commercially available hand creams) to study the structure development of emulsions under shear stress.

The results prove an ability of the investigated emulsions to repair the damage caused by mechanical impacts over time.

The Rheonaut offers a new approach to rheology by providing molecular insight and can thus reveal information about molecular organization and dynamics under deformational flow.

The exact knowledge of the interacting fundamental structuring mechanisms creates the basis for an optimized tuning of technical, process engineering, and material parameters with respect to a functionally optimized structuring of emulsion systems.

## References

- [1] Saiki, Y. and Prestidge, C.A., Korea-Australia Rheol. J. 17 (2005), 191-198
- [2] Mason, T.G., Curr. Opin. Colloid Interface Sci. 4 (1999), 231-238

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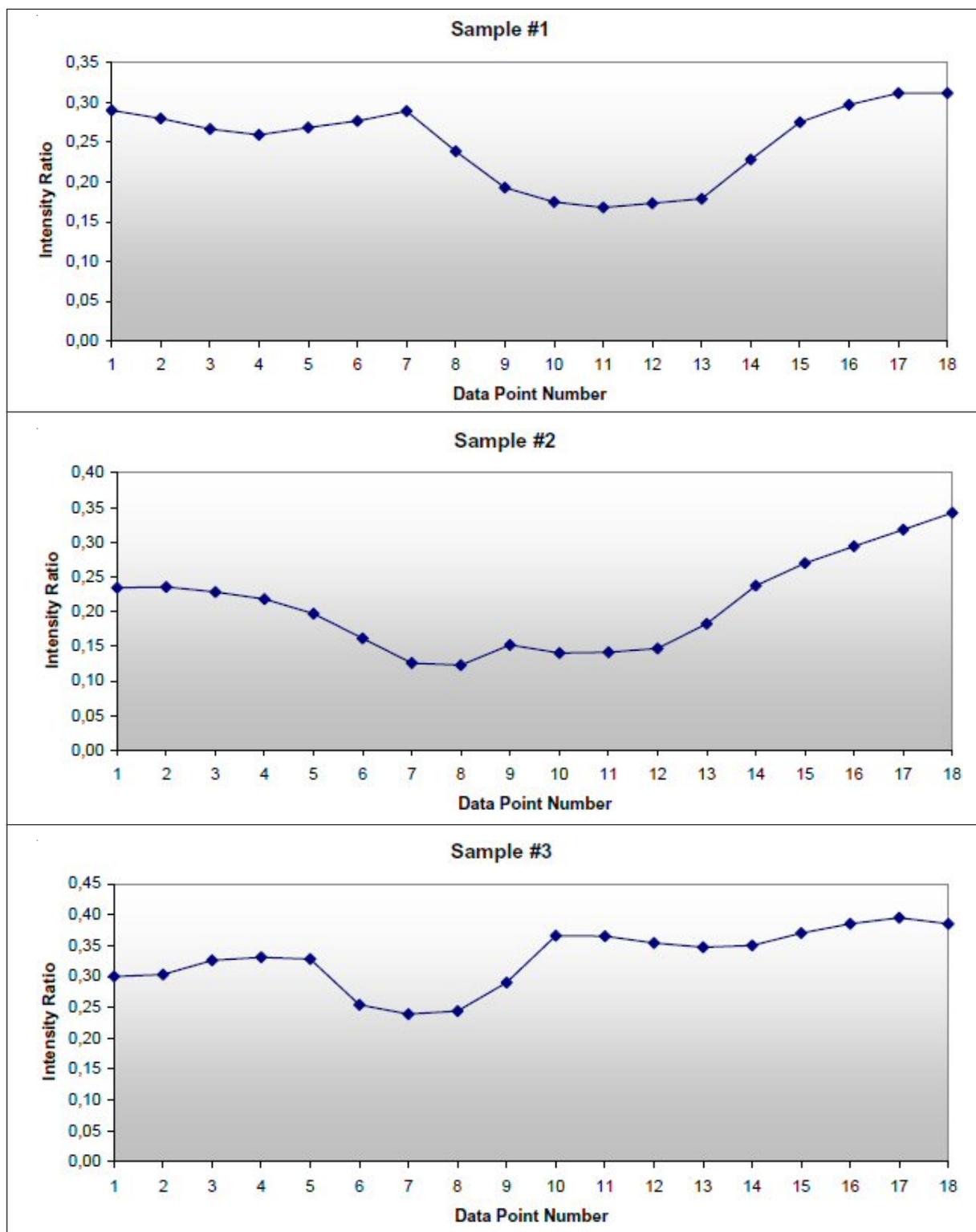


Fig. 5: Absorption ratio ( $3354\text{ cm}^{-1}/2922\text{ cm}^{-1}$ ) from each FT-IR spectrum plotted against the data point number.

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