Case study

# Interfacial Rheology as Foam and Emulsion Stability Indicator

Stabilizing emulsions is a significant problem for example in foods [1], personal care products, and pharmaceuticals [2]. Then, on the other hand, there are cases where emulsion stability is unwanted and de-emulsification is needed such as in oil industry [3].

Interfacial dilatational rheology has been shown to influence emulsion stability, particularly drop coalescence and Ostwald ripening [4], and the pulsating drop method, or oscillating drop method, has become a powerful technique for measuring interfacial dilatational rheology in the past couple of decades [5] [6].

The technique builds on the well-established pendant drop method. The pendant drop volume oscillates, causing the interfacial area to regularly compress and dilate which likewise compresses and dilates the adsorbed film at the liquid-fluid interface. The response in interfacial tension to changes in the area of the drop allows for calculating the interfacial dilatational elasticity and viscosity.

From the measured interfacial tension data, the surface dilatation modulus E as well as its elastic E′ (storage) and viscous E′′ (loss) components can be calculated according to the equation

$$E = E' + E'' = \frac{d\gamma}{dlnA} = E_0 + i\omega\eta$$

The dilatational storage modulus (E′) is related to the elasticity of the adsorbed film whereas the dilational loss modulus (E′′) takes into account the relaxation mechanism occurring at the interface.

## Case study: Interfacial elasticity as droplet stability predictor in microfluidics

Droplet, or droplet-based microfluidics have gained a lot of attention during the past decade or so. There, two immiscible liquids are flown through a microfluidic channel so that the other one is a continuos phase (i.e. the liquid where the droplet flows) and the other one is the dispersed (i.e. droplet) phase. The main benefits of using such a system is to ability to handle

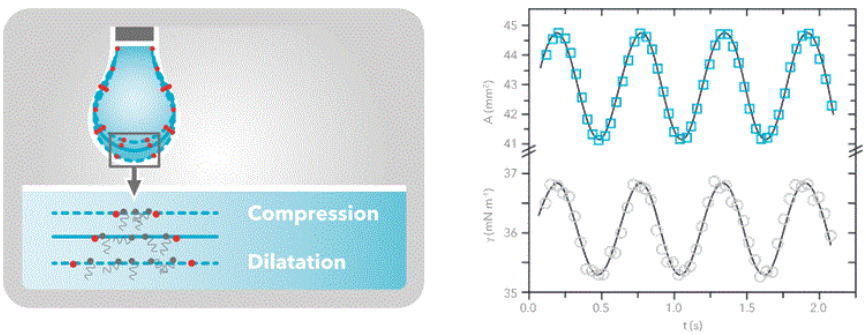


**Figure 1.** The oscillation of the surface area of the drop causes oscillation of the interfacial tension with the same frequency.

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**Figure 2**. Theta Pulsating drop for interfacial rheology measurements

miniature volumes, have better control over mixing, sorting and encapsulation and the possibility to do high-thoughput analysis. Applications vary from single cell analysis to nanodevice fabrication [7].

In these applications, the droplets must remain stable and not coalesce or else the analysis or reactions can be ruined. The choice of continuous phase, droplet phase, and additives heavily influences drop stability, but making the best choice of components is not trivial. Interfacial tension measurements are commonly made, but these are poor predictors of drop stability. Often formulations are simply run through the microfluidic system to see if they are successful. This can not only take a long time, but the materials can be expensive and limited.

**Purpose of the study** was to measure interfacial dilatational rheology for quality control (QC) of microfluidic device formulations. Changes in the oil or aqueous phase formulations have been identified as causes of failure in the microfluidic system, and a reliable and cost-effective QC method is needed. The previous QC method involved testing the real microfluidic system with different formulations, which was expensive and time consuming. As an alternative, we demonstrate that interfacial elasticity measurements using the pulsating drop method is a time- and cost-effective quantitative QC method for distinguishing successful and poor-performing systems.

**Measurements were performed** with Theta Pulsating drop (Fig. 2) . Drops of fluorinated oil which are common filler fluids in microfluidics were suspended from a 22-gauge stainless steel needle with volumes between 200 nl -1 µl (Fig. 3). The oil was surrounded by an aqueous phase which contained proteins and other biomolecules. Eight different oil formulations were studied and the aqueous phase remained constant. After forming the drop, 5 min elapsed so that an equilibrium interfacial tension was reached. Then the drop oscillated sinusoidally at 0.1, 0.2, 0.5 and 1.0 Hz with a change in interfacial area of approximately 10%. Images of the drop were recorded and analyzed in OneAttension to determine the interfacial tension and area in each image. The resulting interfacial tension and area versus time data were further analyzed in OneAttension to automatically generate the elastic and viscous components of the complex interfacial dilatational modulus.

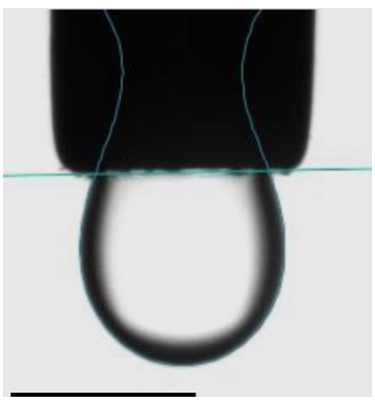

**Figure 3**. An example pendant drop of sample 3 with the best fit of the Young - Laplace equation (blue line) and automatically detected needle tip (green line). The scale bar is 0.5 mm.

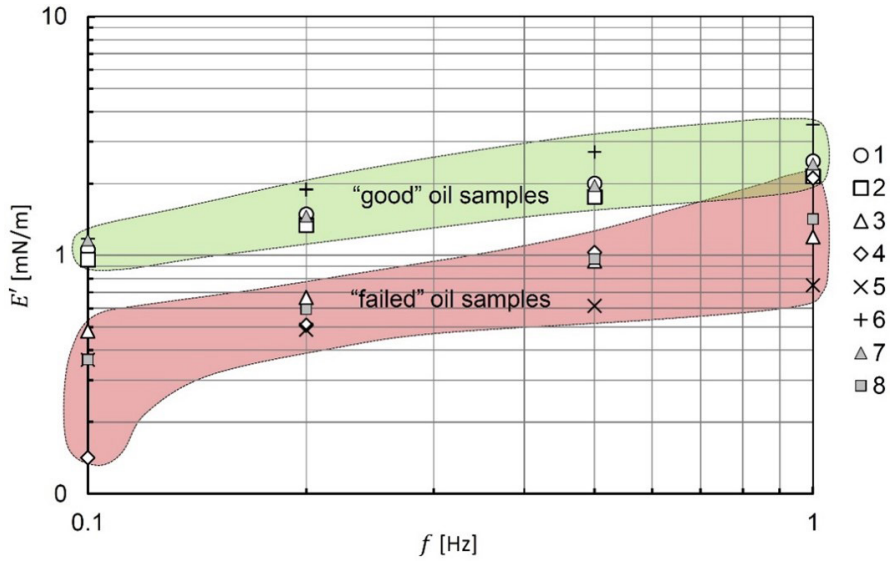


**Figure 4**. The interfacial elasticity (E') is plotted versus frequency for all eight samples on a log-log plot, Samples determined to be "good" resulting in stable drops are circled in green, and samples that "failed" are circle in red.

## Results

The resulting interfacial elasticity E' is plotted for all eight samples in Fig. 3. Clear separation between two sample groups is observed in this plot. Specifically, samples 3, 4, 5, and 8 are grouped and have lower E', while samples 1, 2, 6, and 7 are grouped and collectively have higher E'. Generally, a higher elasticity corresponds to a drop that is more stable and less likely to coalesce. When drops coalesce, the process is similar to the rupture of thin films. When the film is more elastic, it is better suited to resist rupture or coalescence. Indeed, samples 1, 2, 6, and 7 were revealed to perform best in the real system, whereas the other samples gave poor performance. To better distinguish the two groups of samples in Fig. 4, the "good" samples are circled in green and the "failed" samples are circled in red. Therefore, it can be seen that the interfacial elasticity, and specifically a higher elasticity, is an indicator for drop stability. This result agrees with similar observations from the literature [4].

## Conclusions

In this note we demonstrated that interfacial elasticity measurements using an Attension Theta Pulsating drop can distinguish systems with stable drops from systems with drops that are prone to coalesce. Thus, by establishing pass/fail criteria, these measurements can be used for quality control as a quick, quantitative, and cost-effective solution. For example, based on the results shown in Fig. 4, if measurements are made at 0.1 Hz the criterion for passing the sample could be E^'>0.8 mN/m. The principles demonstrated here can be applied outside of droplet-based microfluidics as well, to food emulsions, pharmaceuticals, personal care products, and oil and gas emulsions.

## References

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