# DROPLET FAILURE MODES: CAUSES, UNDERLYING EFFECTS AND AMELIORATION STRATEGIES

A. Debon,<sup>1</sup> R.C.R. Wootton<sup>1</sup> and K.S. Elvira<sup>1\*</sup>

<sup>1</sup>Institute for Chemical and Bioengineering, Department of Chemistry and Applied Biosciences ETH Zürich, SWITZERLAND

## ABSTRACT

This study describes in detail twenty phenomena that cause microfluidic droplets to differ from the spherical and self-contained reaction vessels required for microfluidic applications. We classify these failure modes into families depending on the underlying effects (surface-, surfactant- or shear-based) and have developed numerical and qualitative models to explain the cause of each failure mode. The models are based on extensive experimental data gathered from over 40 combinations of commonly used oil/surfactant systems and the examination of their effect on both droplet formation and droplet stability over time. Finally, these data and models can be used to determine possible amelioration strategies.

KEYWORDS: Droplets, Leakage, Surfactant.

### **INTRODUCTION**

Droplet microfluidic technology has found applicability in fields varying from high-throughput diagnostics to chemical synthesis.[1] Therefore, the formation of monodisperse droplets, and their shortand long-term stability and storage, form a crucial research question. There has been little previous work in this area, especially in the field of surfactant chemistry and polydimethylsiloxane (PDMS) surfacebased effects. Surfactants are widely used and yet the choice of surfactant is generally based on qualitative rather than quantitative reasoning.[2] Likewise, PDMS is the most commonly used substrate material for microfluidic devices,[3] and yet we show that it has less than ideal surface stability regarding long-term wetting, for example. Our work is the first to provide an in-depth study of multiple oil/surfactant combinations, what droplet failure modes they cause, why they happen and what can be done to mitigate them.

# EXPERIMENTAL

For this work, we designed a PDMS microfluidic device where droplets could be subjected to common microfluidic actions: creation at a T-junction, mixing in a channel motif designed to induce bakers deformation, release into a larger chamber (to assess the effect of close proximity and reduction in flow rates), exit from the chamber (increased flow rates and compression) and storage in a large chamber with a section including a pillar network (open *versus* confined storage conditions). Oils used included FC-40, FC-770, mineral oil, silicone oil, decane, hexadecane and soybean oil. Surfactants included EA surfactant,[4] Span 80 and ABIL EM 90, amongst others. Additionally, surface treatments and storage conditions were also varied. To ensure that valid comparisons could be made, each oil/surfactant system was tested in an identical, but newly manufactured, microfluidic device and all devices were fabricated following an exact methodology.

#### **RESULTS AND DISCUSSION**

Figure 1 shows most of the droplet failure modes observed, from those commonly reported in literature (e.g. tip-streaming) to the entirely novel (e.g. substrate-driven droplet deformation). We have data to show that these failure modes affect all oil/surfactant systems, even such commonly used systems as FC-40 and EA surfactant. Our data show that these failure modes detrimentally affect the integrity of droplets both during formation and during storage. Because of the high surface-area-to-volume ratios typical in droplet systems, fouling or cross-contamination that occur due to these failure modes will have a disproportionally large effect on the integrity of the experimental data gathered using these systems.



Figure 1: Images of the droplet failures modes identified in this study, with arrows highlighting them when necessary. Droplet failure modes caused by wetting and surface affinity in flow are co-flow, dripping mode, generalised surface-driven droplet deformation, localised surface-driven droplet deformation, tip-streaming, wetting and localised adhesion; and substrate-driven droplet deformation

occurs during droplet storage due to wetting and surface affinity effects. Failure modes caused by shear forces and interfacial tension are droplet splitting, satellite droplet formation and beading. Failure modes that occur due to surfactant effects in flow are micelle formation, droplet interface bilayer (DIB) formation, droplet adhesion and surfactant-monolayer interactions, while raft-driven droplet deformation and budding occur during droplet storage also due to surfactant effects. The tertiary phase formation failure mode occurs due to the phase properties of the system during droplet storage.

## CONCLUSION

We believe that this work represents a crucial insight into the physics and chemistry of droplet integrity and long-term storage and hope that this study will become a fundamental reference for microfluidic droplet research.

## REFERENCES

- [1] K.S. Elvira, X. Casadevall i Solvas, R.C.R. Wootton and A.J. deMello, "The past, present and potential for microfluidic reactor technology in chemical synthesis", *Nat. Chem.*, 5, 905-915, 2013.
- [2] J.-C. Baret, "Surfactants in droplet-based microfluidics", Lab Chip, 12, 422-433, 2012.
- [3] J. Zhou, A.V. Ellis and N.H. Voelcker, "Recent developments in PDMS surface modification for microfluidic devices", *Electrophoresis*, 31, 2-16, 2010.
- [4] C. Holtze, A.C. Rowat, J.J. Agresti, J.B. Hutchison, F.E. Angilè, C.H. Schmitz, S. Köster, H. Duan, K.J. Humphry, R.A. Scanga, J.S. Johnson, D. Pisignano, D.A. Weitz, "Biocompatible surfactants for water-in-fluorocarbon emulsions", *Lab Chip*, 8, 1632-1639, 2008.

## CONTACT

\*K.S. Elvira; phone: +41 44 633 9468; katherine.elvira@chem.ethz.ch