Fundamental aspects of microfluidic liquid-liquid phase extraction
and thermally controlled generation of liquid crystal microdroplets

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1. Introduction

- The binary mixture of methanol (MeOH) and the liquid crystal 4-Cyano-4'-pentylbiphenyl (SCB) has the unique property of temperature dependent miscibility. The mixture undergoes a phase transition from a miscible mixture at high temperature to a phase separated system at low temperatures.
- MeOH/SCB systems have been shown to be amenable to liquid-liquid phase extractions on a microfluidic scale where traditional extraction based extraction is not practical. It is simple to selectively extract polar or nonpolar compounds from an initial homogeneous mixture.

- During a previous study carried out by Dr. Stuart Ibsen at UCL, droplet formation was observed during the early stages as the homogenuous mixture was cooled. The droplets subsequently were observed to coalesce followed by phase separation into two distinct layers. However, little was known about the fundamental phase separation mechanism between the two liquids.

- Motivation:
  - Understand the conditions that initiate droplet formation, understand the underlying principles and achieve close control over the droplet size.
  - A second objective is to control the droplet formation in flow inside a microfluidic environment, using a cooled metallic tip to induce locally the phase separation within the mixture. A microfluidic device was entirely designed to explore this possibility.

2. Materials

- 4-Cyano-4'-pentylbiphenyl (SCB)
- MeOH/SCB: SCB is classified as a thermosensitive liquid crystal, i.e. the arrangement of the mesogens is temperature dependent. Even if the SCB was used as a complex solvent, it is particularly interesting as a liquid crystal because the transition from an isotropic phase to a nematic phase occurs around room temperature, making the tuning of its properties feasible at near-room operating conditions.
- Pluronic F-127

3. Fluorescent Microscopy

- Observations made at the early stages show that the liquid crystal 5CB is phase separated into a MeOH-rich and a SCB-rich phase, consistent with literature reports.
- Observation made at the final stage show that the phases are phase separated into a MeOH-rich and a SCB-rich phase, consistent with literature reports.

4. Microfluidic device for temperature stimulated droplet formation

- Device design:
  - Transparent polyvinyl chloride (PVC): chemical resistance to methanol.
  - Designed with AutoCAD 2016 software, channels milled by an engraving machine and two PVC chips are thermally bonded together.
  - Copper tip is inserted via a sapphire channel and coated with AmTech epoxy resin: good thermal insulation.
  - End of the copper tip is embedded in a neoprene rubber o-ring: accurate T control.

- Device operation:
  - Lab temperature 27°C: prevent mixture phase separation.
  - MeOH/SCB 75/25: preferred for droplet formation.

- Results:
  - Observation of individual liquid crystal droplets. Temperature decrease → more droplets formed.
  - Influence of the cooling zone instead of having droplets nucleating from the tip.

5. Surfactant for droplets stabilization

- Motivation:
  - Prevent the coalescence of SCB liquid crystal droplets and the mixture to phase separate in two different layers. Useful for chemical components or liquid crystal confined.

- Method:
  - MeOH/SCB 75/25 w/w with Pluronic F-127 powder incorporated
  - Heated at 35°C and cooled-down at 15°C at 20°C/Min
  - Images were recorded with bright light using the upright microscope.

- Results:
  - Pluronic F-127 acts as a surfactant, decreasing the interfacial tension between both phases and stabilizes the liquid crystal SCB droplets.
  - Decreasing the Pluronic content: higher volume content of liquid crystal droplets.
  - Droplets stabilized in the very early stages.

6. Conclusion

- Two different phase separation mechanisms can be expected, depending on the MeOH/SCB composition and both consistent with a sphidroal decomposition mechanism.
  - MeOH/SCB 80/20: cocrystallizing SmA phase of SCB and O-MeOH.
  - MeOH/SCB 75/25: sectioning SmA phase of SCB droplets into a methanol-rich phase domain.

- The understanding of the MeOH/SCB mixture phase separation mechanism could help to tailor a more efficient microfluidic liquid-liquid phase extraction. In particular for the Diamos European H2020 project, where the mixture is used to detect the chemotherapeutic drug concentration of Doxorubicin (Dox) within blood.

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8. References