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# Production of Concentrated Pickering Emulsions with Narrow Size Distributions using Stirred Cell Membrane Emulsification

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Abstract: Stirred cell membrane emulsification (SCME) has been employed to prepare concentrated Pickering oil in water emulsions solely stabilized by fumed silica nanoparticles. The optimal conditions under which highly stable and low polydispersity concentrated emulsions using the SCME approach are highlighted. Optimization of the oil flux rates and the paddle stirrer speeds are critical to achieving control over the droplet size and size distribution. Investigating the influence of oil volume fraction highlights the criticality of the initial particle loading in the continuous phase on the final droplet size and polydispersity. At a particle loading of 4 wt%, both the droplet size and polydispersity increase with increasing of the oil volume fraction above 50%. As more interfacial area is produced the number of particles available in the continuous phase diminish and coincidentally a reduction in the kinetics of particle adsorption to the interface resulting in larger polydisperse droplets. Increasing the particle loading to 10 wt%, leads to significant improvements in both size and polydispersity with oil volume fractions as high as 70% produced with coefficient of variation values as low as ~30% compared to ~75% using conventional homogenization techniques.

Keywords: Pickering Emulsions; Concentrated Emulsions; Stirred Cell; Membrane Emulsification; Controlled Droplet Size

## **INTRODUCTION**

Concentrated emulsions consist of tightly packed liquid droplets with a microscopic liquid film in between the droplets.<sup>1</sup> Concentrated emulsions are widely used the production of a variety of products ranging from mayonnaise, cosmetic creams, emulsion based explosives and the production of low density polymer foams.<sup>2-5</sup>

Surfactants are generally used in large quantities in the continuous phase to stabilize concentrated emulsions against coalescence.<sup>6</sup> The use of large quantity of surfactants has potential environmental drawbacks and is costly. In addition careful selection of the surfactant is needed to ensure that phase inversion does not occur especially with temperature.<sup>7</sup> An alternative is to stabilize emulsions using colloidal particles as emulsifiers known as Pickering emulsions<sup>8</sup> that offer several advantages. The particles are able to achieve high attachment energies to the interface and are irreversibly attached once adsorbed.<sup>9</sup> In addition the particles can deliver multi-functional product benefits such as pigments in cosmetics and personal care emulsions.

A key challenge in particle-stabilized emulsion is the kinetics of particle adsorption to the newly formed interface. Nanoparticles are inherently larger when compared to low molecular surfactants and therefore have small diffusion coefficient values and thus long adsorption times.<sup>10, 11</sup> Furthermore, the process of adsorption can be considered as an energy activated process dictated by a) the particle collision frequency with interface, b) particle adherence to the interface and c) displacement wetting.<sup>12</sup> Therefore to ensure successful particle adsorption events leading to sufficient droplet coverage for emulsion droplet stability is highly dependent on a) particle concentration, b) double layer interactions between the droplet and particle, and c) the contact angle made by the particle at the liquid-liquid interface.

Emulsions are conventionally produced using high shear mechanical processes that require inefficient high energy inputs. The limitations in using such techniques are that the emulsions are created with little or no control over the droplet size distributions. An alternative to these high shear techniques is to use drop by drop production techniques. Highly monodisperse Pickering emulsions have been produced using microfluidics<sup>13-15</sup> one droplet at a time which can be a limitation regarding overall throughput. This can be addressed by setting up multiple parallel

devices to improve overall throughput, however occasional blockages are hard to spot and resolve.<sup>16</sup>

Membrane emulsification provides an alternative capability of producing near-monodisperse emulsion droplets at a high throughput level compared to microfluidics. In membrane emulsification the dispersed phase is expressed through a porous membrane with well-defined pores into a continuous phase containing the emulsifier. The droplets detach from the membrane surface by the aid of shear forces (direct membrane emulsification) due to either a crossflow of the continuous phase acting on the membrane surface,<sup>17, 18</sup> membrane rotation<sup>12, 19</sup>, membrane vibration<sup>20-22</sup>, mechanical stirring<sup>23, 24</sup> or by pulsing the continuous phase over the membrane surface.<sup>25</sup> In the absence of shear, droplets can be spontaneously detached using surface tension<sup>26</sup> from pore outlets (premix membrane emulsification) at very low disperse phase throughputs.<sup>27</sup>

Concentrated emulsions (dispersed volume fraction >30%) have been produced using both direct and premix membrane emulsification methods.<sup>25, 28-30</sup> Holdich *et al.*<sup>25</sup> produced O/W emulsions stabilized with Tween 20 with dispersed volume fractions of 45% v/v in a single pass by pulsing the continuous phase to achieve a droplet size distribution with a span value of 0.4. The key to producing such high disperse phase volumes was due to the decoupling of the shear stress from the cross-flow velocity. The droplet size was primarily controlled by the shear stress whereas the cross-flow velocity was used to recover the droplets and did not assist in droplet generation. This allows for production of concentrated emulsions without high shear conditions that can damage shear sensitive components and break large droplets that are formed. Shimoda *et al.*<sup>28</sup> used a crossflow membrane emulsification rig to produce emulsions with a disperse phase content of 40% in a single pass using SDS (Sodium Dodecyl Sulfate) with typical span values of 0.45 - 0.64. Suzuki and Hagura<sup>29</sup> reported the preparation of highly concentrated emulsions from low

concentration pre-emulsified emulsions by the membrane phase inversion method. Both the oil and water phases contained surfactants. The maximum concentration obtained was ca. 90% for O/W emulsion, and ca. 85% for W/O emulsion with coefficient of variation values of  $\sim 0.1$ . Koris *et al.* used a mechanically modified crossflow membrane emulsification apparatus to produce O/W emulsions stabilized with Tween 80.<sup>30</sup> The modification allowed a greater shear stress to be imposed at the membrane surface and emulsions with oil volume fraction of 38% was achieved via long-term emulsification.

The majority of concentrated emulsions produced using membrane emulsification are stabilized using surfactants as emulsifiers. In contrast, studies demonstrating the use of particle stabilizers in producing highly concentrated emulsions have utilized high shear mixing environments.<sup>31-38</sup> The authors are unaware of any previous work that have studied the preparation of concentrated Pickering emulsions using membrane emulsification techniques. Herein, in this paper low polydispersity concentrated emulsions with dispersed phase volume fractions of up to 70 vol% are prepared and optimized using fumed silica particles as stabilizers in conjunction with a stirred cell membrane emulsification (SCME) system. Fumed silica particles was chosen as a candidate system as they are readily available, extensively investigated and thus well characterized. In addition their surface properties can be easily modified to achieve different contact angles at the liquid-liquid interface which is an important parameter in Pickering emulsions.

## **MATERIALS AND METHODOLOGY**

**MATERIALS.** The partially hydrophobic silica nanoparticles modified by reacting with hexadecylsilane (Aerosil R816, 10 - 12 nm, specific surface area BET =  $190 \pm 20 \text{ m}^2 \text{ g}^{-1}$ ) were purchased from Evonik Industries, Germany.<sup>39</sup> All the following chemicals were used as received;

tricaprylin oil (purity  $\geq 99\%$ , Sigma-Aldrich), isopropanol (IPA, purity  $\geq 99\%$ , Acros Organics) and sodium chloride (NaCl, purity  $\geq 99\%$ , Sigma-Aldrich).

## **EXPERIMENTAL**

*Preparing nanoparticle dispersion:* The silica nanoparticles (4 wt%) were prepared in 0.1M NaCl (Sigma-Aldrich, U.K., 99%) in distilled water (resistivity 18.2 M $\Omega$  cm, ~pH 5.8 - 6.2) and sonicated in an ultrasound bath (Jeken PS-D30, 180 W power, ~40 kHz operating frequency) for 30 minutes prior to use. The use of 0.1M NaCl and a solution pH of 6 was chosen based on previous membrane emulsification work based on silica particles.<sup>12</sup>

*Preparation of concentrated Pickering emulsions using homogenizer:* Emulsions of varying disperse phase volume fractions were prepared using an IKA T25 Ultra-Turrax homogenizer operating at 12 000 rpm for 5 mins. Emulsions were made to a total volume of 10 mL containing the desired oil and water volume fractions to prepare the concentrated emulsions.

*Preparation of concentrated Pickering emulsions using Stirred Cell Membrane Emulsification (SCME):* Emulsification studies were performed using a stirred cell equipped with hydrophilic nickel disc membrane (Micropore Technologies Ltd., Hatton, Derbyshire, U.K.). A 24 V DC motor is used to drive a paddle stirrer above the membrane surface to create shear. According to the manufacturer, applying a voltage in the range of 4 to 15 V results in paddle stirrer speeds of 500 – 1900 rpm. The relationship between the applied voltage and the stirrer speed is linear. The nickel disc membrane used had a pore size of 20  $\mu\text{m}$  with a spacing of 200  $\mu\text{m}$ . The oil injection rate was controlled using a syringe mounted on a syringe pump (Razel A99FMZ, Fisher Scientific, U.K.). For the experiments reported here oil flow rates from 0.01 to 0.50 mLmin<sup>-1</sup> were examined corresponding to disperse fluxes of 0.66 to 33 Lm<sup>-2</sup>h<sup>-1</sup>.

Before concentrated emulsions were prepared, experiments were initially performed to obtain the optimum oil injection rate and paddle stirrer speed for creating low polydisperse droplets. In these experiments the stirred cell was filled with 90 mL of the nanoparticle dispersion at a particle concentration of 4 wt%. Once 10 mL of oil (i.e. a total emulsion volume of 100 mL) had passed through the membrane, both the pump and the agitator were switched off and the droplets were collected and analyzed.

In the case of concentrated emulsions the total emulsion produced was also 100 mL, however the volume fractions of the continuous phase and disperse phase were varied to achieve the desired volume fraction of dispersed phase in the emulsion. All the emulsification experiments were undertaken at room temperature.

*Emulsion Characterization:* The droplet size distribution and droplet diameter, was evaluated using a laser diffraction particle size analyzer (Malvern Mastersizer) equipped with a small volume Hydro 2000SM sample dispersion unit (~50 mL). After each measurement, the cell was rinsed once with isopropanol, followed by three rinses with distilled water. The glass walls of the cell were carefully wiped with lens cleaning tissue to avoid contamination across the samples.

For each emulsion, three separate samples and measurements were performed and the mean average of these is reported. The particle size was taken as the volume mean diameter ( $D_{4,3}$ ) and the coefficient of variation (CV) was calculated from the standard deviation ( $\sigma$ );

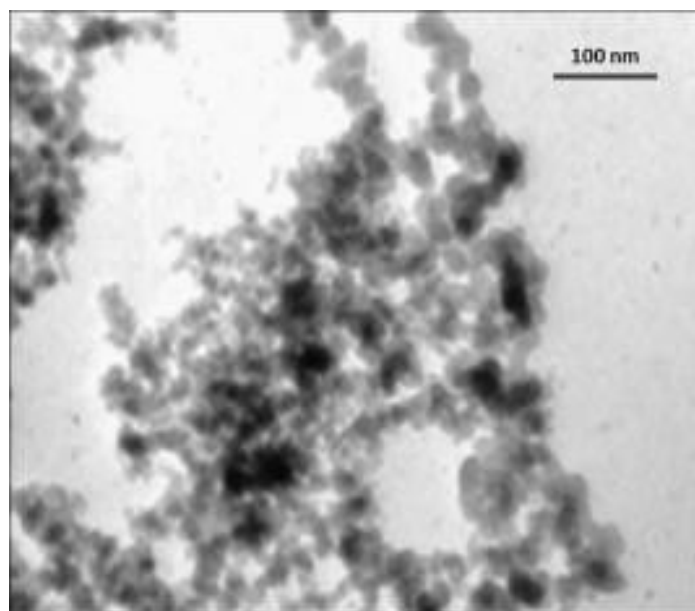
$$CV (\%) = (\sigma/D_{4,3}) \times 100$$

The emulsions were also characterized via optical microscopy using an Olympus BX51TF microscope with a built in camera and Olympus Cell<sup>^</sup>D imaging software.

## RESULTS AND DISCUSSION

The aim of this work was to investigate the use of SCME to produce concentrated tricaprylin oil in water Pickering emulsions with good control over both droplet size and droplet size distribution using silica nanoparticles (Figure 1). The composition and properties of the o/w emulsions can be found in Table 1. Although the primary particle size of the particles was 12 nm they did aggregate in solution. Zeta potential measurements of the dispersions, their aggregation behavior is presented in Figures S1 and S2 in the supplementary information. Tricaprylin oil was selected as it has been shown to previously produce stable emulsions with silica particles<sup>12, 40</sup> and was also confirmed by bulk emulsion studies presented in Figure S3 of the supporting information. The figure also shows that having the dispersions at pH 6 and 0.1 M NaCl leads to greater emulsion stability compared to lower electrolyte concentrations. Furthermore it has also been shown that triglyceride based oils adsorb onto both silicic acid and silica hydrogels via hydrogen bonding between the hydrogen atom in the silanol groups and the ester carbonyl groups.<sup>41, 42</sup> It should however be noted that silica nanoparticles have been used to stabilize emulsions with other oils such as n-hexadecane<sup>43</sup> and n-dodecane.<sup>44</sup>

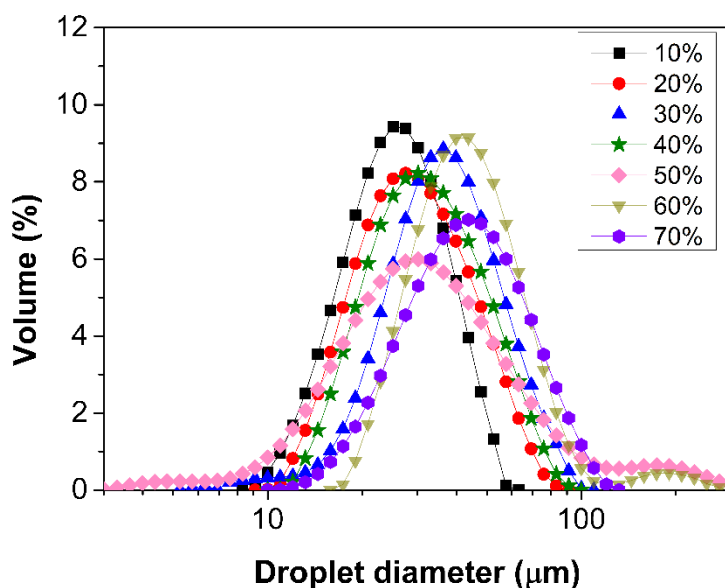
Prior to using the SCME, concentrated emulsions were made using an Ultra Turrax homogenizer. The silica nanoparticle dispersion concentration was fixed at 4 wt% to ensure comparison with the SCME work reported later (although a 10 wt% dispersion was prepared in some of the latter SCME experiments to investigate the influence of particle concentration). The droplet size distribution of concentrated emulsions produced is presented in Figure 2.



**Figure 1.** TEM micrograph of Aerosil R816 silica nanoparticles dispersed in 0.1M NaCl electrolyte solutions.

**Table 1.** Composition and properties of O/W emulsions presented in this work.

Aqueous (continuous) Phase	~12 nm Aerosil R816 Silica particles dispersed in 0.1M NaCl electrolyte solution
Density of Continuous Phase	1030 kg m <sup>-3</sup> @4wt% and 1060 kg m <sup>-3</sup> @10wt%
Oil (dispersed) Phase	Glyceryl Trioctanoate (Tricaprylin)
Viscosity of Oil @20°C	26 mPa. s
Density of Oil	956 kg m <sup>-3</sup> @20°C

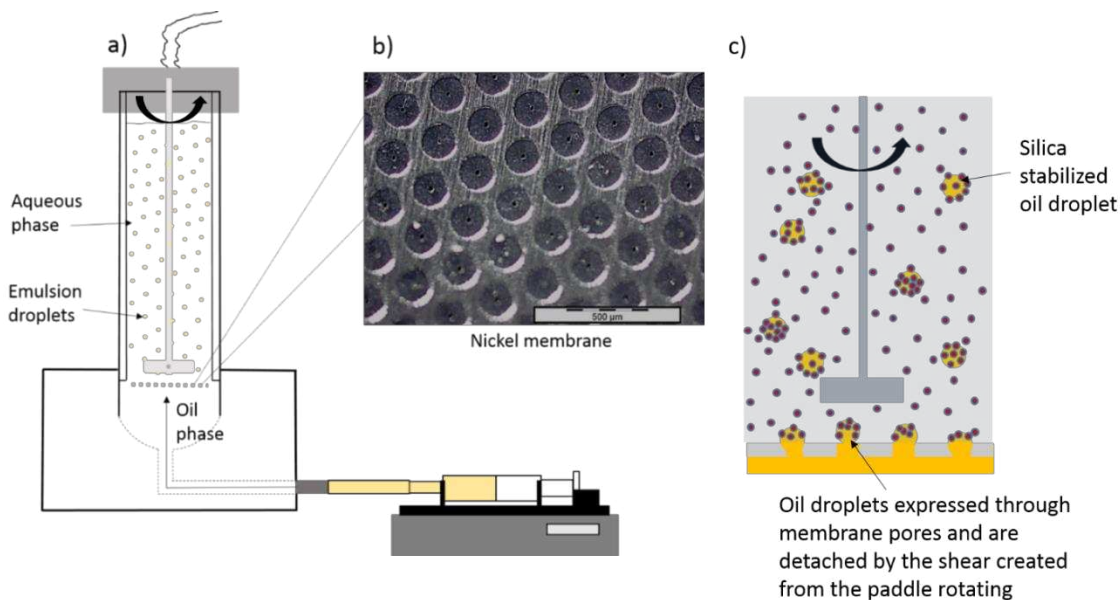


**Figure 2.** Droplet size distribution of tricaprylin oil in water emulsions at different oil volume fractions created using Ultra-Turrax homogenizer. The aqueous phase contained a 4 wt% dispersion of 12 nm silica nanoparticles in 0.1 M NaCl and at a pH = 6.

The droplet size distributions of the emulsions created with the Ultra-Turrax homogenizer are very broad due to the variability in high shear environments used to prepare such emulsions which gives poor control over droplet size distribution even if the mean size can be controlled. CV values from these emulsions created were between 60-75%. It was anticipated that the drop-by-drop production employed by the SCME would offer greater control of producing concentrated emulsions but with narrower size distributions.

The emulsions were produced with a commercial SCME. The cell setup is illustrated in Figure 3a with close-up image of the membrane in Figure 3b. Prior to conducting the experiments the membrane was cleaned extensively; firstly with washing-up liquid, then ethanol and finally with

distilled water. The membrane was then wetted with the continuous phase before the dispersed phase was pushed through.

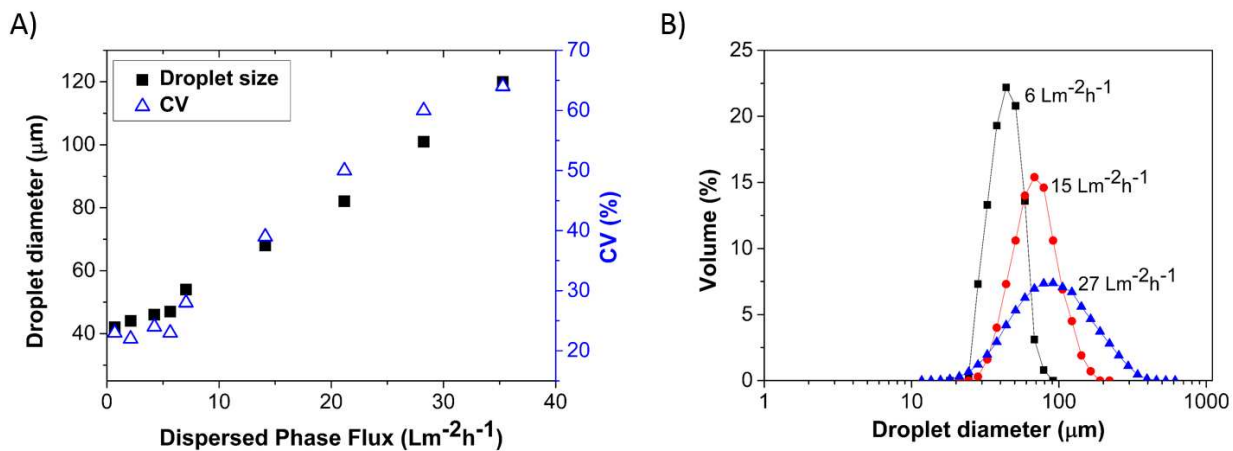


**Figure 3.** a) Schematic illustration of the stirred cell membrane emulsification rig, b) optical micrograph of the 20 μm hydrophilic nickel membrane used in this study and c) formation and detachment of oil droplets expressed through the porous membrane into the continuous phase containing silica nanoparticles that adsorb onto the oil/water interface.

Initial experiments were designed on finding the optimal oil injection rate and paddle stirrer speed that allowed the greatest control over droplet size and in particular the size distribution. These optimal conditions were then utilized to prepare concentrated emulsions of varying oil volume fractions.

Data for the mean droplet diameter as a function of dispersed phase flux and the resulting CV at a fixed paddle speed of 1019 rpm (8 V) is presented in Figure 4a. The overall trend shows that as

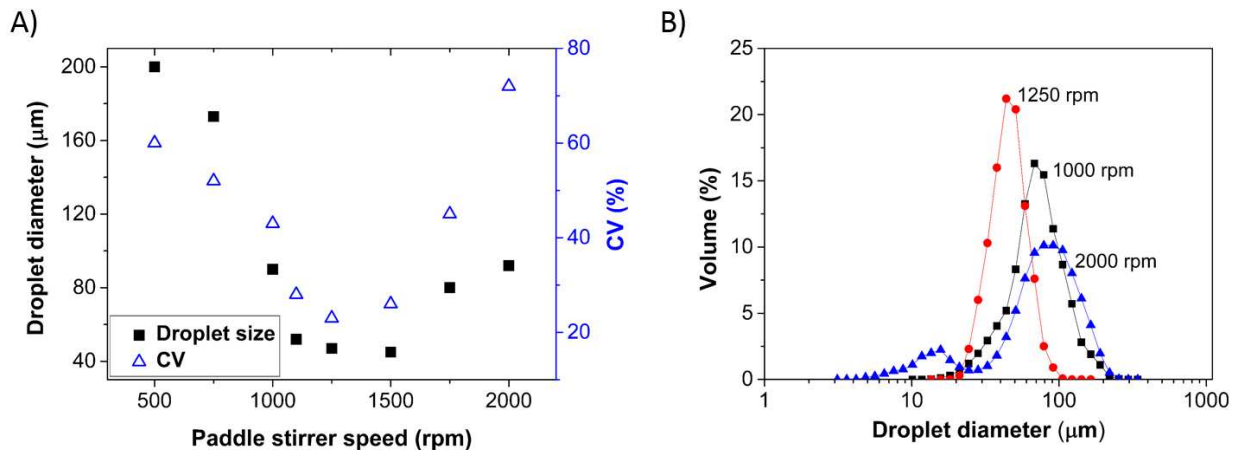
the oil flux increases the droplet size also increases. This is because the shear rate over the membrane surface is fixed, and thus change in the oil flux is directly related to change in the generation of new interfacial area as a function of time.<sup>45-47</sup> The data does suggest that there is a critical oil flux of  $6 \text{ Lm}^{-2}\text{h}^{-1}$  at a fixed shear rate. At this flux value and below, oil droplets of 40 to 60  $\mu\text{m}$  are produced with CV's less than 30%. Increasing the flux above this value, the CV values start to increase sharply as can also be seen by the droplet size distribution presented in Figure 4b. This is typical behavior of membrane emulsification operation as increasing the flux value produces droplets much faster (becoming larger at the membrane surface before subsequent detachment) and kinetics of emulsifier adsorption will determine the stability and polydispersity of the droplets created.<sup>12, 24, 48</sup> This defines an upper limit, above which there is poor control over the droplet distribution.



**Figure 4:** a) Variation in the mean droplet diameter of tricaprylin oil in water prepared using SCME as a function of dispersed phase flux. The aqueous phase contained a 4 wt% dispersion of 12 nm silica nanoparticles in 0.1 M NaCl and at a pH = 6. Paddle stirrer speed was kept constant at 1019 rpm (8 V), b) Droplet size distribution for emulsions prepared at 6, 15 and 27  $\text{Lm}^{-2}\text{h}^{-1}$ . The oil volume fraction produced was 10%.

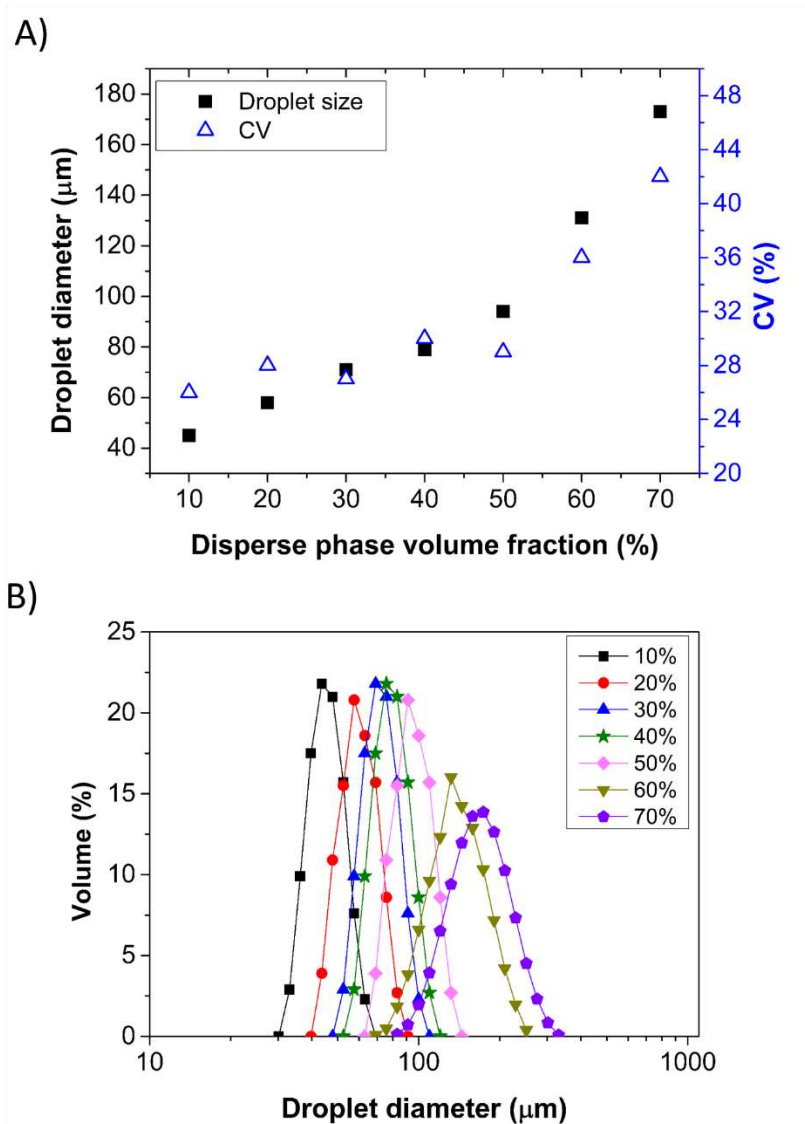
The influence of membrane surface shear was also investigated by changing the paddle stirrer speed above the disc membrane as shown in Figure 5. In principle increasing the stirrer speed increases the lateral shear stress above the membrane surface and should lead to a reduction in the droplet diameter as they are detached from the membrane surface much quicker. In practice, the droplet size and well as the CV did decrease with increasing paddle stirrer speed but up to a critical value (1500 rpm) (Figure 5a). Droplets with CV values as low as 20-30% were achieved at paddle stirrer speeds between 1100 and 1500 rpm. Increasing the stirrer speed above 1500 rpm to 2000 rpm resulted in an increase in droplet size with CV values increasing significantly to ~70%. Droplet size distributions using laser diffraction illustrate how the droplet size distribution is affected by the paddle speed in Figure 5b. It is clear that at 2000 rpm the droplet distribution is bimodal, due to the presence of very small droplets which lead high CV values and thus an increase in the polydispersity of the emulsion. The polydispersity experienced at 2000 rpm can be explained by; i) partial droplet breakage of large droplets into smaller ones or, ii) intensive droplet deformation prior to detachment from the membrane pore, which can lead to the droplets interacting with the membrane surface and membrane wetting.<sup>48, 49</sup> This matches similar observations with previous membrane emulsification work investigating the influence of shear.<sup>12,</sup>

19, 45



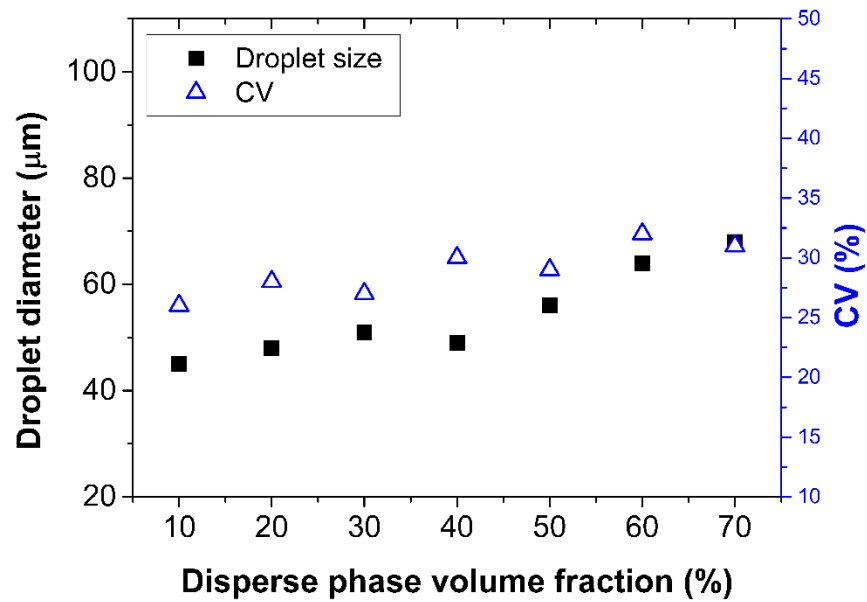
**Figure 5:** A) Variation in the mean droplet diameter of tricaprylin oil in water prepared using SCME as a function of paddle stirrer speed. The aqueous phase contained a 4 wt% dispersion of 12 nm silica nanoparticles in 0.1 M NaCl and at a pH = 6. The dispersed phase flux was kept constant at  $6 \text{ Lm}^{-2}\text{h}^{-1}$ . B) Droplet size distribution for emulsions prepared at 1000, 1250 and 2000 rpm. The oil volume fraction produced was 10%.

Optimal conditions from the experiments above were then used to prepare emulsions of varying oil volume fractions up to 70%. In these experiments the paddle stirrer speed and the dispersed phase flux were kept constant at 1250 rpm and  $6 \text{ Lm}^{-2}\text{h}^{-1}$  respectively. The influence of increasing the dispersed phase volume fraction on the mean droplet size and CV is presented in Figure 6.



**Figure 6.** A) Variation in the mean droplet diameter of tricaprylin oil in water prepared using SCME with increasing oil volume fraction. The aqueous phase contained a 4 wt% dispersion of 12 nm silica nanoparticles in 0.1 M NaCl and at a pH = 6. The paddle stirrer speed and dispersed phase flux was kept constant at 1250 rpm and 6 Lm<sup>-2</sup>h<sup>-1</sup>, respectively. B) Droplet size distribution for emulsions as a function of increasing oil volume fraction.

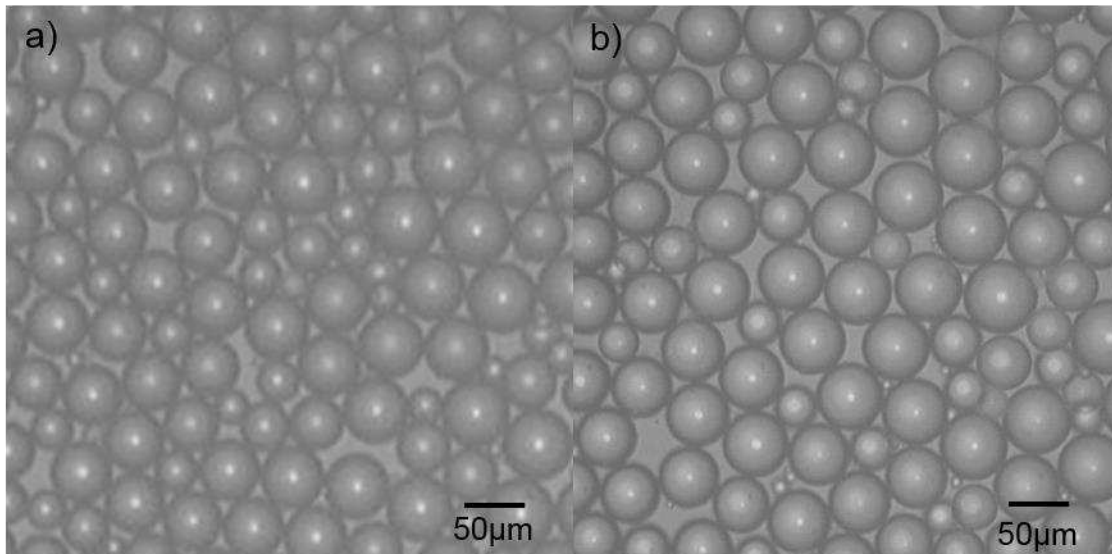
The general trend observed in Figure 6a is that the mean droplet size increases with increasing oil volume fraction. It is interesting to note that between 10 to 50 vol% oil although the droplet size steadily increases the CV values are similar between 25-30%. Above 50 vol% oil there is a large increase in both the droplet size and CV. This is further evident from the droplet size distribution data presented in Figure 6b that shows broadening of the size distributions at 60 and 70 vol% oil. In these experiments, the shear force driving detachment of the droplets is constant and so a change in oil volume fraction equates directly to a change in the production of new interfacial area which needs to be stabilized by the particles in continuous phase that is kept fixed at a concentration of 4wt%. Simple calculations (provided in the supplementary information, S4) show that even for oil volume fractions of 50 vol% and above there are enough particles in the continuous phase to stabilize the new interfacial area (with a monolayer of particles). Therefore increase in droplet size as the oil volume fraction reaches 50 vol% and above is potentially explained by the kinetics of particle adsorption. With the generation of new interfacial area the particles need to not only collide with the interface but undergo successful adsorption events. This collision frequency and successful adsorption event will most likely reduce as new interfacial area is produced, due to the reduction in the number of particles available in the bulk. Therefore as the interfacial area increases the kinetics of adsorption become slower and thus the droplets grow to a larger size before they are stabilized by the particles to impart long term stability.



**Figure 7.** Variation in the mean droplet diameter of tricaprylin oil in water with increasing oil volume fractions. The aqueous phase contained a 10 wt% dispersion of 12 nm silica nanoparticles in 0.1 M NaCl and at a pH = 6. The paddle stirrer speed and dispersed phase flux was kept constant at 1250 rpm and  $6 \text{ Lm}^{-2}\text{h}^{-1}$ , respectively.

To investigate if the particle loading in the continuous phase could improve the mean size and CV especially at the higher oil volume fractions the continuous phase was loaded to a particle concentration of 10 wt%. This was to ensure that at higher oil volume fractions the number of particles were far in excess compared to the number needed to improve the kinetics of particle adsorption. The paddle stirrer speed and dispersed phase flux were kept the same as before. Figure 7 illustrates the variation in mean droplet size with oil volume fraction at this new particle concentration. By increasing the particle concentration to 10 wt% the mean droplet size and CV values in particular are very similar across all the oil volume fractions investigated as illustrated in Figure 8. This makes sense since increasing the particle loading even at 70 vol% oil compared

to 4 wt% helps in ensuring that the interface is stabilized against coalescence which decreases the polydispersity of the emulsion droplets.



**Figure 8:** Optical micrographs of tricaprylin oil droplets at different oil volume fractions; a) 20 vol% and b) 70 vol%. The aqueous phase contained a 10 wt% dispersion of 12 nm silica nanoparticles in 0.1 M NaCl and at a pH = 6. The paddle stirrer speed and dispersed phase flux was kept constant at 1250 rpm and  $6 \text{ Lm}^{-2}\text{h}^{-1}$ , respectively.

The concentrated Pickering emulsions are more uniform than ones produced using high shear homogenizers since the droplets are produced in a controlled manner. In addition the SCME allows the preparation of concentrated emulsions at a convenient scale to test new and exotic emulsifiers before scaling up to larger membrane emulsification rigs such as cross-flow systems especially when dealing with expensive materials.

## **CONCLUSIONS**

We report the production of concentrated emulsions with oil volume fractions as high as 70% stabilized using 12 nm colloidal silica using a stirred cell membrane emulsification rig. Initial work to optimize the production conditions (based on an oil volume fraction of 10%) show that careful control of the dispersed phase and paddle stirrer speed is needed. This is because the flux controls the production of new interfacial area as a function of time, whilst the stirrer speed controls the shear profiles above the membrane surface. Emulsion droplets produced during the optimization stage had CV values as low as 23% and when the oil fraction was increased the CV values depended on the particle loading in the continuous phase. With the higher particle loading (10 wt%), emulsion droplets with CV values between 25 - 30% were achievable.

## **ASSOCIATED CONTENT**

### **Supplementary Information**

S1. Silica nanoparticle charging behaviour, S2. Aggregation behavior of the silica nanoparticles, S3. Bulk emulsion studies and S4. Impact on emulsion formation.

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## **AUTHOR INFORMATION**

### **Author Contributions**

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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