Supplementary Information

Exploring effects of polymeric stabiliser molecular weight and concentration on emulsion production via stirred cell membrane emulsification

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Preliminary experiments to determine dispersed phase ideal dispersed phase pump rate

Initial optimisation experiments were performed to determine the ideal dispersed phase pump rate to investigate the impact of varying the properties of the stabilising polymer. These experiments were performed as outlined in the method section of the main manuscript using 2% LMw-PVA-88 solution as the aqueous phase at pump rates between 0.01 and 1 mL/min.
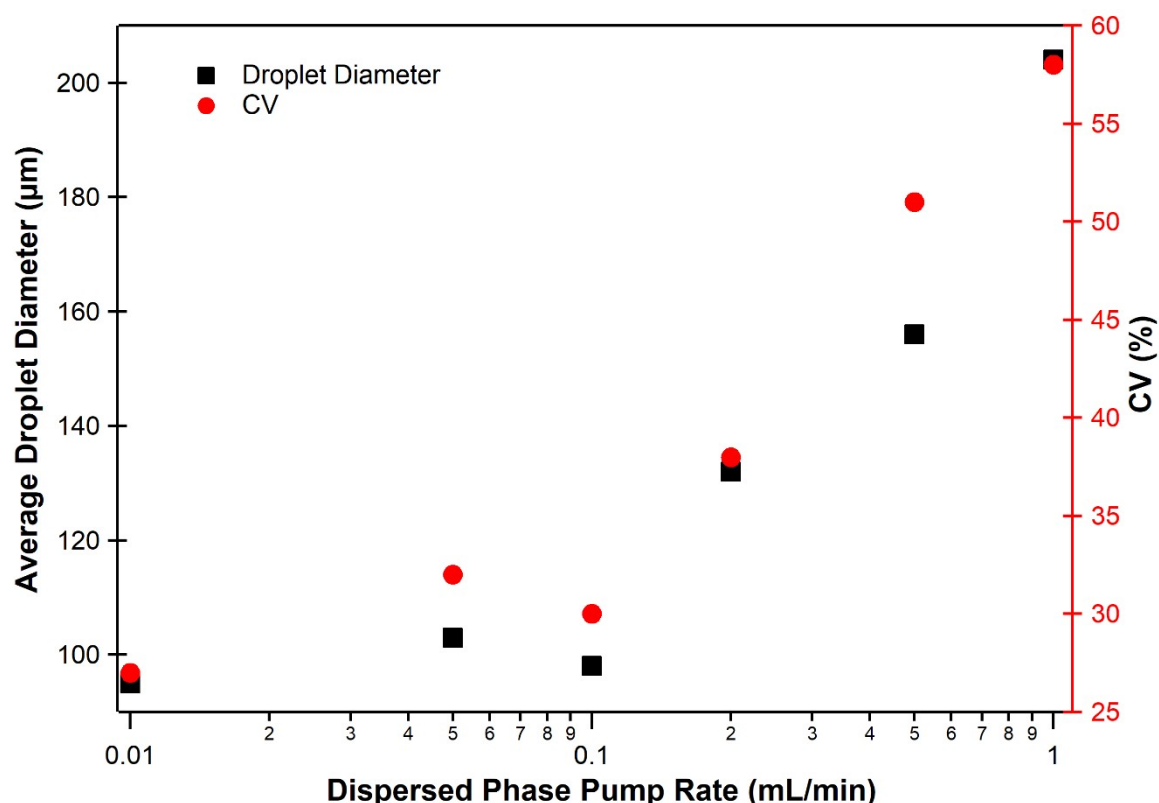

Figure S1. Average droplet diameter and coefficient of variation of dodecane in 2% LMw-PVA-88 emulsions produced via membrane emulsification as a function of oil (dodecane) pump rate.

All experiments above 0.1 mL/min resulted in emulsions with large average droplet sizes and very wide size distributions (high CV). As such, those conditions were deemed unsuitable to investigate the impact of polymeric stabilisers on the emulsion properties. At 0.01 mL/min the smallest and most well controlled emulsions were produced. However, the time required for the process given the very slow pump rate and was not practical for investigation as each run would require approximately 17 h. Therefore, 0.1 mL/min was deemed the most suitable pump rate for further investigation as using these parameters resulted in the best (lowest CV %) emulsions within the investigated parameter space.

Membrane emulsification using polyvinyl alcohol with high hydrolysis degree

Emulsions were prepared as outlined in the main manuscript. However due to the poor surface activity of the highly hydrolysed (hydrophilic) polymer stability was poor. From Figure S2 millimetre sized droplets were observed for the HMw polymer and very large size distributions were observed for both 99% hydrolysed samples.
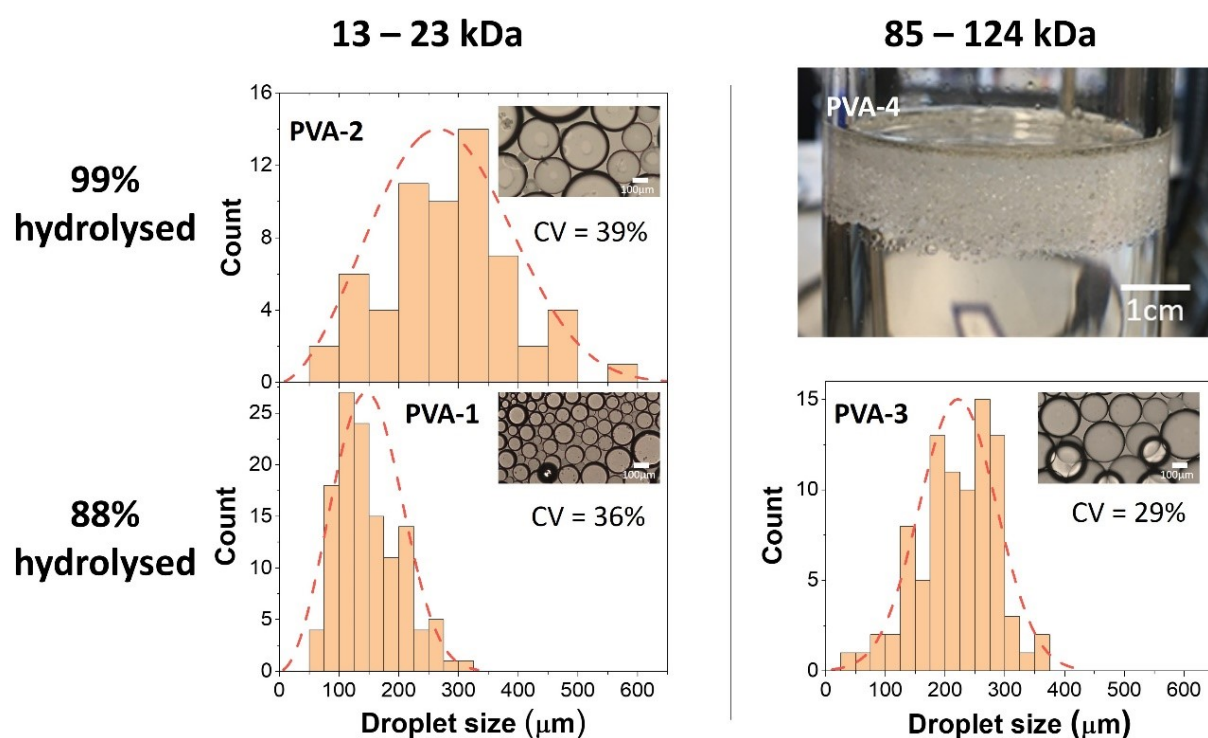

Figure S2. Influence of two different polymer molecular weight and hydrolysis degree on the droplet size distributions and coefficient of variation of the resulting n-dodecane in water emulsions prepared using a hydrophilic nickel disc membrane (Micropore Technologies Ltd., Redcar, U.K.). A 24 V DC motor was used to drive a paddle stirrer above the membrane surface to create the necessary shear for droplet detachment. The nickel disc membrane used had a pore size of 20 μm with a pitch of 200 μm, and the flowrate was 0.1 mL/min. The histograms and plotted distributions (dashed line) are based on image analysis of several hundred droplets. Insets show example optical micrographs of the emulsion droplets in each condition. The image for the emulsions stabilised with the 99% hydrolysed high MW polymer is that of the emulsion itself, which shows millimetre droplets visible with the naked eye.

The polymer concentration used for all emulsions was 0.1 wt%.

Calculations of values presented in Table 2 and Table S1

Droplet lifetime was calculated bases on the volumetric flowrate provided by the syringe and the number of pores with an assumed active pore rate of 2%.[1]

Based on a flow rate of 0.1 mL/min from the syringe,

$$Volumetric\ Flowrate\ across\ membrane\ = 1.67 \times 10^{-9}\ m^3 \cdot s^{-1}$$

The membrane used in this work contained 126,000 pores (based on 20um pore size, 200um pitch, porosity 0.9%[1]) and an assumption was made that 2% of the pores were active at any given time, which falls within typical values used in the literature[2].

$$Volumetric\ flowrate\ per\ pore\ = \frac{1.67 \times 10^{-9}}{0.02 \times 12600} = 6.63 \times 10^{-13}\ m^3 \cdot s^{-1}$$

Based on the droplet radius of 60 μm as calculated from IFT values obtained from Figure 4 and Equation 3 in the main manuscript

$$Volume\ of\ droplet\ detaching\ from\ pore = \frac{4}{3}\pi(6 \times 10^{-5})^3 = 9.05 \times 10^{-13}\ m^3$$

$$\therefore Droplet\ lifetime\ on\ pore = \frac{9.05 \times 10^{-13}\ m^3}{6.63 \times 10^{-13}\ m^3 \cdot s^{-1}} = 1.4\ s$$

Properties of highly hydrolysed polyvinyl alcohol polymers used in experiments

Here we present an expanded version of Table 2 in the main manuscript. These data are calculated using Equation 3 in the main manuscript. Although not discussed in detail in the main manuscript it is instructive to consider the impact of the chemical nature of the stabilising polymer and energetic implications. This is demonstrated and explained below with reference to the percentage of highly hydrophilic hydrolysed moieties on the PVA molecules of comparable Mw to those discussed in the main manuscript.

Table S1. Expanded values from Table 2 including values obtained for highly hydrolysed polymers.

(1) PVA Sample	(2) Radius of Gyration (nm)	(3) Calculated inter-polymer chain distance (nm)	(4) Time taken to diffuse distance in column (3) (ms)	(5) Predicted droplet diameter at equilibrium IFT value (μm)	(6) Lifetime of droplet on membrane pore (based on droplet size in column (5) (s)	(7) Predicted droplet diameter and for a bare oil-water IFT value (~53 mN/m) (μm)	(8) Lifetime of droplet on membrane pore (based on droplet size in column (7) (s)
LMw-PVA-88	4.8 - 6.5	69 - 92	0.056 - 0.13	120	1.4	220	8.5
LMw-PVA-98	5.1 - 6.9	72 - 96	0.062 - 0.15	130	1.7	220	8.5
HMw-PVA-88	13- 15	177 - 214	0.91 - 1.6	124	1.5	221	8.5
HMw-PVA-99	13 - 16	186 - 225	1.1 - 1.9	135	1.9	221	8.5

For LMw-PVA-98 with a radius of gyration of ~5 – 7 nm, the polymer chain diffusion time is up to 10 times lower than the droplet lifetime on the membrane surface. However due to the hydrophilic character the adsorption is weak and not sufficient to stabilise the interfacial area. This therefore results in droplet coalescence and leads to a broad size distribution until sufficient coverage and consequent steric stabilisation occurs. When using HMw-PVA-99, due to the larger radius of gyration (~13 - 16 nm) the polymer diffusion rate is slower than that of the smaller polymers but still faster than the droplet production rate. However, not all contacts between the polymers and the droplet surface result in an adsorption event, which likely means that upon droplet detachment the PVA coverage at the interface will still be low and thus obtaining an equilibrium IFT value will be very unlikely. Furthermore, the

hydrophilic nature of the polymer molecules will lead to weak adsorption once at the interface, meaning droplet coalescence will prevail giving rise to the large milli-meter sized droplets seen during experimentation and in Figure S2. Using PVA chains that are more hydrophobic in nature i.e. 88% (contains 12% acetate groups) the distribution of the polymer radius of gyration is slightly smaller (compared to those at 99% hydrolysis degree) and thus the associated diffusion time from the bulk to the interface will be faster. More importantly, the adsorption will be energetically more favourable when compared to the highly hydrolysed sample, thus leading to more effective stabilisation.

Stability of Emulsions prepared with ultra-turrax after 60 minutes

Emulsions were prepared again and allowed to stand for 60 minutes prior to beginning measurements (120 minutes total since emulsification). This was performed in order to more reliably compare the emulsion behaviour to that of the membrane emulsification system which requires approximately 100 minutes in total.
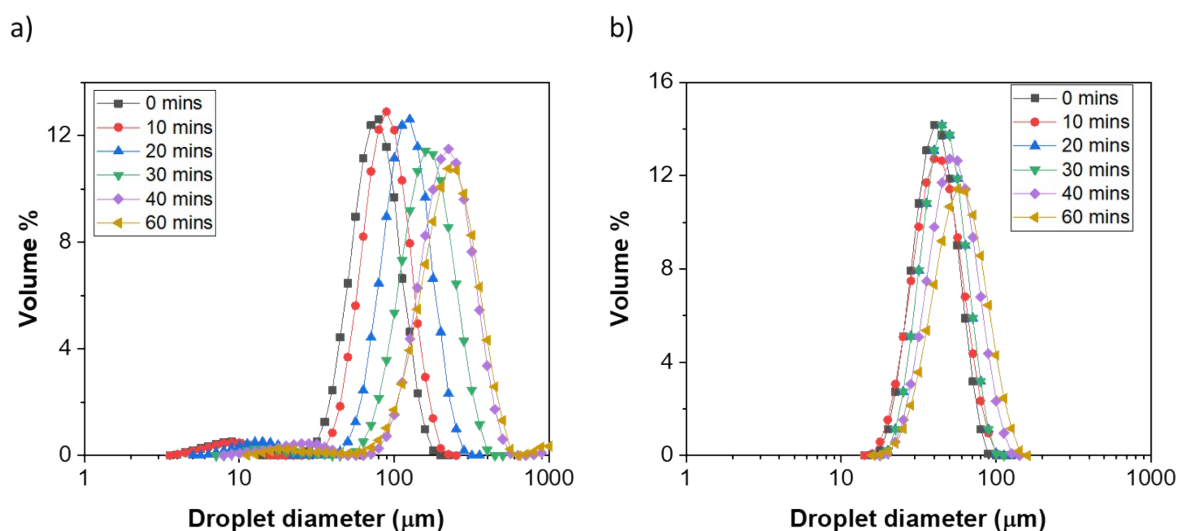
a)

b)

Figure S3. Droplet size distribution of n-dodecane in water emulsions stabilised with 0.1 wt% (a) LMw-PVA-88 and (b) HMw-PVA-88. The emulsions were prepared via high shear homogenisation at 12,000 rpm for 2 mins and then allowed to stand for 1 hour (which corresponds to t = 0 mins). The emulsions are then measured to track the droplet size evolution over a period of 60 mins.

References

1. E. Egidi, G. Gasparini, R. G. Holdich, G. T. Vladisavljević and S. R. Kosvintsev, J. Membr. Sci., 2008, 323, 414-420
2. G. T. Vladisavljević and Schubert H., Desalination, 2002, 144, 167-172.