Controllable Monodisperse Multiple Emulsions

From Soft-Matter

Contents

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Controllable Monodisperse Multiple Emulsions

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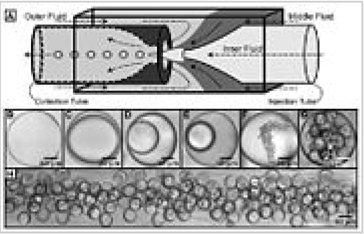
Key Contribution

Multiple emulsions, in which dispersed drops contain smaller drops inside, are useful in a large number of commercial applications, including chemical synthesis and drug delivery. For many of these applications, it is critical to have control over the size and structure of multiple emulsion systems. The structure of multiple emulsion systems is in this case defined as the number of bubbles contained in each size "level" of larger bubbles.



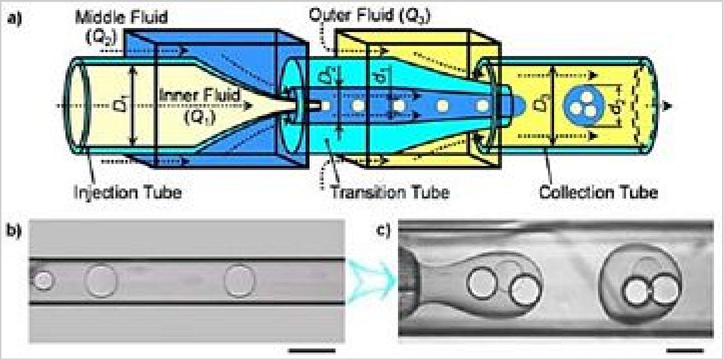
A microcapillary device was used to make double emulsions in Utada *et al.* (Science **308**:537). (A) Device schematic. B-E) Double emulsions with a single inner drop. (F-G) Double emulsions with many inner drops. (H) A group of double emulsion drops, each containing a single inner drop.

Standard bulk emulsification techniques break up drops with shear or impact stresses generated by mechanical agitation (aka vigorous shaking); unfortunately, these methods produce polydisperse emulsions of poorly controlled geometries. Some groups have been able to control shear by using porous membranes or microchannels, and to create multiple emulsions by iterating the process. This class of technologies allows a fine control of the emulsion volume fraction, but is unable to control the structure.

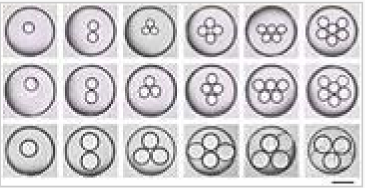
Utada *et al.* (Science **308**:537) showed that a microcapillary device could be used to make double emulsions consisting of a single droplet encapsulated in another droplet. Their device could make emulsions of a highly defined size, but had difficulties controlling structure. Additionally, the device could not make higher-dimensional emulsions (such as triple emulsions.

In this paper, Chu *et al.* build on the techniques in Utada *et al.* by separating the emulsification steps into multiple stages. The result is the first system that is able to create monodisperse emulsions with defined structures.

Double Emulsions



A device that makes controlled monodisperse double emulsions. (A) Device schematic. (B)First emulsification stage. (C) Second emulsification stage. Scale bar = 200 µm

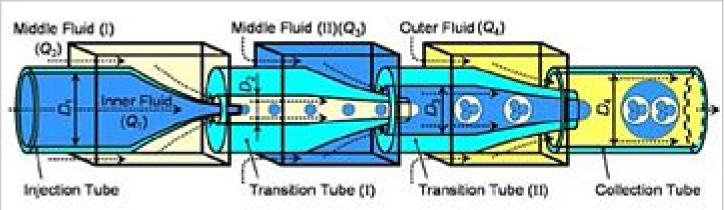


Monodisperse double emulsions made by varying the flow rates of the fluids while using the same device. Scale bar = 200 µm.

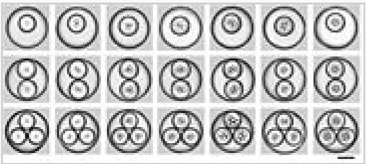
The capillary device shown in the image above was made from polyethylene tubing, syringes, a Harvard Apparatus syringe pump, and a high-speed camera attached to a microscope. The circular injection and transition tubes were housed in 1 mm inner diameter (ID) square tubes. The ID of the transition tube was 200 µm, and the ID of the collection tube was 580 µm. 100 cSt polydimethylsiloxane (PDMS) was the outer fluid, which formed the bulk phase of the emulsion; 2 %wt Dow Corning 749 fluid (http://www.dowcorning.com/applications/search/products/details.aspx?prod=02705338&type=PROD) was added to the PDMS and acted as a surfactant. The middle fluid, which formed the larger droplets, was an solution of 10 %wt glycerol and 2% (w/v) polyvinyl alcohol (PVA). The inner fluid, which formed the emulsions housed in the larger glycerol/PVA emulsions, consisted of 10 cSt PDMS oil.

By adjusting the flow rates of each fluid it was possible to control the structure of the emulsion. The coefficient of variation (CV), which is the ratio of the standard deviation of the size distribution to its arithmetic mean, was <2.3% for the inner dropplets and <1.6% for the larger droplets.

Triple Emulsions



A schematic of the device used to generate controlled monodisperse triple emulsions.



Monodisperse triple emulsions. Scale bar = 200 µm

To make triple emulsions a transition tube containing a different fluid was added to the double emulsion-generating device. The innermost fluid was, 10 %wt glycerol, 2% (w/v) PVA. The outer middle fluid (middle fluid II) was 10% wt glycerol, 2% (w/v) PVA, 11.3% (w/v) of the monomer N-isopropylacrylamide (NIPAM), 0.8% (w/v) of the co-monomer sodium acrylate, 0.77% (w/v) of the crosslinker N,N'-methylenebisacryamide (BIS), 0.6% (w/v) of the initiator ammonium persulfate (APS). The inner middle fluid (middle fluid I) was 10 cSt PDMS oil, 5 %wt Dow Corning 749 fluid, 8% (v/v) of the accelerator N,N,N',N'-tetramethylethylenediamine (TEMED). The outer fluid was, as before, 100 cSt PDMS with 2 %wt Dow Corning 749 fluid. The ID of the first transition tube was 200 µm and the ID of the second transition tube was 250 µm. The other geometrical parameters were the same as in the double emulsion device.

As with the double emulsion device, the emulsion geometries could be controlled by adjusting flow rates. The CV of the diameters were <1.5%, showing that the device could precisely control drop sizes.

Control of Drop Diameter

The ability to precisely regulate fluid flow rates gave control over the number of inner droplets in a double emulsion system (N_1):

$$N_1 = \frac{f_1}{f_2}$$

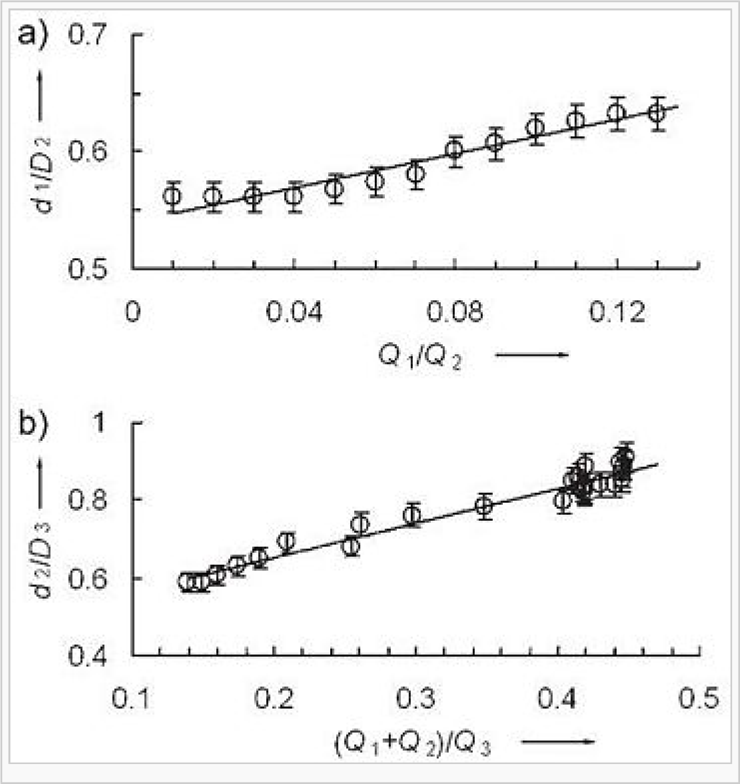
Where f_1 and f_2 are the formation rates of the inner and outer droplets, respectively. The diameters of the inner (d_1) and outer drops (d_2) can be measured by optical micrography, and can be used to calculate the droplet formation rates.

$$N_1 = \frac{\frac{Q_1}{\frac{\pi}{6}d_1^3}}{\frac{Q_1+Q_2}{\frac{\pi}{6}d_2^3}} = \frac{Q_1}{Q_1+Q_2}\frac{d_2^3}{d_1^3}$$

Experiments showed that the scaled drop diameters are proportional to the scaled flow rates:

$$\frac{d_1}{D_2} = a_1\left(Q_1/Q_2\right) + b_1$$

$$\frac{d_2}{D_3} = a_2\left(\frac{Q_1+Q_2}{Q_3}\right) + b_2$$



Substituting the experimental fits for d_1 and d_2 into the equation relating N_1 to flow rate gives:

$$N_1 = \left(\frac{Q_1}{Q_1+Q_2}\right)\left(\frac{D_2^3}{D_1^3}\right)\left(\frac{a_2\left(\frac{Q_1+Q_2}{Q_3}\right)+b_2}{a_1\left(\frac{Q_1}{Q_2}\right)+b_1}\right)^3$$

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