Wetting-Induced Formation of Controllable Monodisperse Multiple Emulsions in Microfluidics

Supplementary material

Nan-Nan Deng, Wei Wang, Xiao-Jie Ju, Rui Xie, David A. Weitz and Liang-Yin Chu

School of Chemical Engineering, Sichuan University, Chengdu, Sichuan, 610065, China.
E-mail: chuly@scu.edu.cn (L.-Y. Chu); Fax & Tel: +86 28 8546 0682
School of Engineering and Applied Sciences, Department of Physics, Harvard University, Cambridge, Massachusetts, 02138, USA
State Key Laboratory of Polymer Materials Engineering, and Collaborative Innovation Center for Biomaterials Science and Technology, Sichuan University, Chengdu, Sichuan, 610065, China

Part I. Supplementary Note

Part II. Supplementary Figures S1-S7.

Part III. Supplementary Movies S1-S3.
Part I. Supplementary Note

Calculation of the spreading coefficients.

In our experiments, the fluids used for wetting-induced formation of double emulsions (Fig. 1) are listed as follows. Fluid A1 is SO containing 1 wt.% PGPR 90, Fluid A2 is SO/Octanol (3:1, v/v) containing 1 wt.% PGPR 90, Fluid B is water containing 1 wt.% SDS, and Fluid C is SiO containing 1 wt.% DC749.

Based on the Eqn (4), conclusions can be drawn as follows: When $\gamma_{BC} > \gamma_{AC} + \gamma_{AB}$, i.e., $S_A$ is always positive, drop A engulfs drop B, forming B/A/C double emulsions (Figure 1a3). This process has no relationship with the radius ratio of $R_A/R_B$. When $\gamma_{AC} + \gamma_{AB} > \gamma_{BC} > \gamma_{AB}$, the engulfing process of drop A and drop B depends on the radius ratio of $R_A/R_B$. The larger the radius ratio of $R_A/R_B$, the smaller value of $\alpha$. As long as $S_A$ is positive, drop A will entirely engulf drop B. When $\gamma_{BC} < \gamma_{AB}$, drop A cannot engulf drop B.

Case 1 (Drop A1 engulfing drop B, as shown in Fig. 1a3):

For drop B and drop A1 dispersed in continuous phase C:

$\gamma_{A1B} = 0.18 \text{ mN m}^{-1}$, $\gamma_{BC} = 3.07 \text{ mN m}^{-1}$, $\gamma_{A1C} = 1.37 \text{ mN m}^{-1}$.

So, $\gamma_{A1B} + \gamma_{A1C} = 1.55 < 3.07$, i.e., $\gamma_{BC} > \gamma_{A1B} + \gamma_{A1C}$.

That is to say, the value of $S_{A1}$ is always larger than 0. Thus, drop A1 can always completely engulf drop B in spite of drop sizes (Fig. 1a3, d, f, g).

Case 2 (Drop B engulfing drop A2, as shown in Fig. 1a4):

For drop B and drop A2 dispersed in continuous phase C:

$\gamma_{A2B} = 0.58 \text{ mN m}^{-1}$, $\gamma_{BC} = 3.07 \text{ mN m}^{-1}$, $\gamma_{A2C} = 3.16 \text{ mN m}^{-1}$.
For $S_B > 0$, we get $R_B/R_{A2} > 0.49$ with the similar derivations in Eqn (1) to (4). That is, when the value of $R_B/R_{A2}$ is larger than 0.49, drop B can completely engulf drop A2, forming A2/B/C double emulsions (Fig. 1a4, e, h, i).
Part II. Supplementary Figures S1-S7:

**Fig. S1.** Wetting-induced formation of double emulsions with controllable core/shell ratios. (a) The schematic of complete spreading of drop A over drop B to form B/A/C emulsions in designed microchannels, in which fluid A is SO containing 1 wt.% PGPR 90, fluid B is water containing 1 wt.% SDS, and fluids C1 and C2 are SiO containing 1 wt.% DC749. (b-d) High-speed optical micrographs of the wetting-induced formation of double emulsions with different core/shell ratios. The flow rates are: (b) \( Q_A = 20 \mu\text{L h}^{-1}, Q_{C1} = 40 \mu\text{L h}^{-1}, Q_B = 200 \mu\text{L h}^{-1} \) and \( Q_{C2} = 300 \mu\text{L h}^{-1} \); (c) \( Q_A = 80 \mu\text{L h}^{-1}, Q_{C1} = 70 \mu\text{L h}^{-1}, Q_B = 150 \mu\text{L h}^{-1} \) and \( Q_{C2} = 300 \mu\text{L h}^{-1} \); (d) \( Q_A = 40 \mu\text{L h}^{-1}, Q_{C1} = 40 \mu\text{L h}^{-1}, Q_B = 150 \mu\text{L h}^{-1} \) and \( Q_{C2} = 500 \mu\text{L h}^{-1} \). Scale bars, 200 \( \mu\text{m} \).
**Fig. S2.** Wetting-induced formation of double emulsions with controllable number of inner drops. (a) The schematic of entire engulfing of drop A by drop B to form A/B/C emulsions in designed microchannels, in which fluid A is SO/Octanol (3:1, v/v) containing 1 wt.% PGPR 90, fluid B is water containing 1 wt.% SDS, and fluids C1 and C2 are SiO containing 1 wt.% DC749. (b-d) High-speed snapshots of the wetting-induced formation of double emulsions with one (b), two (c) or three (d) inner drops. The flow rates are: (b) $Q_A = 50 \mu L \text{ h}^{-1}$, $Q_{C1} = 100 \mu L \text{ h}^{-1}$, $Q_B = 100 \mu L \text{ h}^{-1}$ and $Q_{C2} = 200 \mu L \text{ h}^{-1}$; (c) $Q_A = 80 \mu L \text{ h}^{-1}$, $Q_{C1} = 150 \mu L \text{ h}^{-1}$, $Q_B = 100 \mu L \text{ h}^{-1}$ and $Q_{C2} = 400 \mu L \text{ h}^{-1}$; (d) $Q_A = 90 \mu L \text{ h}^{-1}$, $Q_{C1} = 150 \mu L \text{ h}^{-1}$, $Q_B = 200 \mu L \text{ h}^{-1}$ and $Q_{C2} = 200 \mu L \text{ h}^{-1}$. Scale bars, 200 µm.
**Fig. S3.** Wetting-induced formation of double emulsions with different inner drops. The schematic (a) and high-speed optical micrographs (b) of complete engulfing of two different oil drops by one water drop to form double emulsions with two different inner cores. Fluid A1 is SO/Octanol (3:1, v/v) containing 1% PGPR 90 (w/v) and 1 mg mL\(^{-1}\) LR 300, fluid A2 is SO/Octanol (3:1, v/v) containing 1 wt.% PGPR 90, fluid B is water containing 1 wt.% SDS, and fluids C1 and C2 are SiO containing 1 wt.% DC749. The flow rates are: \(Q_{A1} = 20\ \mu\text{L h}^{-1}\), \(Q_{A2} = 20\ \mu\text{L h}^{-1}\), \(Q_{C1} = 200\ \mu\text{L h}^{-1}\), \(Q_{B} = 150\ \mu\text{L h}^{-1}\) and \(Q_{C2} = 400\ \mu\text{L h}^{-1}\). Scale bar, 200 \(\mu\text{m}\).
**Fig. S4.** Wetting-induced formation of double emulsions with ultra-thin shells and controllable number of inner drops. High-speed optical micrographs of the spreading of one small oil drop over one (a), two (b) or three (c) bigger water drops to form double emulsions with ultra-thin shells and different number of inner cores. The schematic of the microfluidic device is the same as Figure S1a. The flow rates are: (a) $Q_A = 50 \mu$L h$^{-1}$, $Q_{C1} = 100 \mu$L h$^{-1}$, $Q_B = 200 \mu$L h$^{-1}$ and $Q_{C2} = 200 \mu$L h$^{-1}$; (b) $Q_A = 50 \mu$L h$^{-1}$, $Q_{C1} = 100 \mu$L h$^{-1}$, $Q_B = 300 \mu$L h$^{-1}$ and $Q_{C2} = 200 \mu$L h$^{-1}$; (c) $Q_A = 50 \mu$L h$^{-1}$, $Q_{C1} = 200 \mu$L h$^{-1}$, $Q_B = 300 \mu$L h$^{-1}$ and $Q_{C2} = 200 \mu$L h$^{-1}$. Scale bar, 200 $\mu$m.
Fig. S5. Diverse configurations of ultra-thin shelled W/O/O double emulsions with four inner drops. CLSM images of ultra-thin shelled W/O/O double emulsions with four inner drops showing three different configurations as linear (a), planar (b) and tetrahedral (c, d) arrangements. Scale bars, 100 μm.
**Fig. S6.** One O/W/O double emulsion drop completely engulfs two or three O/O single emulsion drops. High-speed snapshots of the complete spreading of one O/W/O double emulsion drop over two (a) or three (b) precursor O/O single emulsion drops to form (O1+O2+O2)/W/O (b) and (O1+O2+O2+O2)/W/O (c) multiple emulsions in detail. The flow rates for case a are: $Q_{A2} = 200 \mu$L h$^{-1}$, $Q_{C(lower)} = 200 \mu$L h$^{-1}$, $Q_D = 150 \mu$L h$^{-1}$, $Q_B = 150 \mu$L h$^{-1}$, and $Q_{C(upper)} = 300 \mu$L h$^{-1}$; and those for case b are: $Q_{A2} = 200 \mu$L h$^{-1}$, $Q_{C(lower)} = 300 \mu$L h$^{-1}$, $Q_D = 150 \mu$L h$^{-1}$, $Q_B = 150 \mu$L h$^{-1}$, and $Q_{C(upper)} = 300 \mu$L h$^{-1}$; and those for Fig. 4e are: $Q_{A2} = 50 \mu$L h$^{-1}$, $Q_{C(lower)} = 100 \mu$L h$^{-1}$, $Q_D = 150 \mu$L h$^{-1}$, $Q_B = 150 \mu$L h$^{-1}$ and $Q_{C(upper)} = 300 \mu$L h$^{-1}$. Scale bars, 200 \mu$m.
**Fig. S7.** One O/O single emulsion drop completely engulfs two O/W/O double emulsion drops. High-speed snapshots of the complete spreading of one O/O single emulsion drop over two O/W/O double emulsion drops to form O/W/O/O triple emulsions with two double emulsion drops as cores in detail. The flow rates are: \( Q_{A1} = 150 \, \mu\text{L h}^{-1} \), \( Q_{C(\text{lower})} = 200 \, \mu\text{L h}^{-1} \), \( Q_{D} = 250 \, \mu\text{L h}^{-1} \), \( Q_{B} = 100 \, \mu\text{L h}^{-1} \) and \( Q_{C(\text{upper})} = 500 \, \mu\text{L h}^{-1} \); and those for Fig. 5c are: \( Q_{A1} = 200 \, \mu\text{L h}^{-1} \), \( Q_{C(\text{lower})} = 200 \, \mu\text{L h}^{-1} \), \( Q_{D} = 150 \, \mu\text{L h}^{-1} \), \( Q_{B} = 150 \, \mu\text{L h}^{-1} \) and \( Q_{C(\text{upper})} = 300 \, \mu\text{L h}^{-1} \). Scale bar, 200 \( \mu\text{m} \).
Part III. Supplementary Movies S1-S3:

**Supplementary Movie S1.** Wetting-induced formation of double emulsions with controllable core/shell ratios.

**Supplementary Movie S2.** Wetting-induced formation of double emulsions with controllable number of inner drops.

**Supplementary Movie S3.** Wetting-induced formation of double emulsions containing different inner drops and triple emulsions.