ChemPubSoc Europe

DOI: 10.1002/cphc.201601334

CHEMPHYSCHEM Articles

# Controlled Generation of Ultrathin-Shell Double Emulsions and Studies on Their Stability

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Double emulsions with a hierarchical core–shell structure have great potential in various applications, but their broad use is limited by their instability. To improve stability, water-in-oil-in-water (W/O/W) emulsions with an ultrathin oil layer of several hundred nanometres were produced by using a microcapillary device. The effects of various parameters on the generation of ultrathin-shell double emulsions and their droplet size were investigated, including the proper combinations of inner, middle and outer phases, flow rates and surfactants. The surfactant in the middle oil phase was found to be critical for the formation of the ultrathin-shell double emulsions. Furthermore, the stability of these double emulsions can be notably improved by increasing the concentration of the surfactant, and they can be stable for months. This opens up new opportunities for their future applications in cosmetics, foods and pharmaceuticals.

## 1. Introduction

Double emulsions, a hierarchical structure of droplets encapsulated in droplets, have attracted significant interest because of their high encapsulation efficiency and controlled release in various applications, including foods, cosmetics, pharmaceuticals and agriculture.[1] Traditional methods of generating double emulsions require a two-step process. For example, to form water-in-oil-in-water (W/O/W) emulsions, primary water emulsions are created in the oil phase, and then the primary emulsion is further emulsified in an outer water phase.[1b,2] This approach lacks control over the structure and size of the resulting double emulsions, which limits their application in controlled encapsulation and release of active components.

With the development of microfluidic technology, double, triple, quadruple and even higher hierarchical emulsions with precisely controlled monodispersity and complexity can now be fabricated by precisely controlling their formation.[3] Among these approaches, the glass capillary device with 3D geometry is one of the most widely used and robust techniques for making complex emulsions.[1a,3c] This method has a number of advantages, such as ease of fabrication, precise modification of local surface and precise control over the internal structure of complex emulsions. Unlike other two-step methods, the glass capillary device generates double and multiple emulsions in a single step, and is able to precisely control the inner- and outer-droplet sizes as well as the number of inner droplets encapsulated inside the outer droplets.[3c]

Double emulsions have great potential in a wide variety of applications. However, the stability of double emulsions, which is essential for practical applications, remains a big challenge due to their inherent thermodynamic instability.[4] For instance, for W/O/W double emulsions, the inner water droplets may coalesce with the continuous aqueous phase and disrupt the double-emulsion structure resulting in the formation of an O/W single emulsion. Therefore, prevention of double-emulsion coalescence and merging remains challenging. One potential way to improve the stability of W/O/W double emulsions is through reduction of the thickness of the middle oil phase; if it is very thin, the lubrication effect significantly slows down the migration of the inner droplet to the outer wall, which is driven by density mismatch, and thus improves the stability.[5] Kim et al. recently developed a simple glass-capillary-based method capable of producing ultrathin-shell double emulsions with a shell thickness of several hundred nanometres.[6] Biodegradable microcapsules of poly(lactic acid)[6] and giant unilamellar lipid vesicles[7] were fabricated by using these ultrathin-shell double emulsions as templates with polymer or lipid dissolved in the middle, oil phase, respectively. Ultrathin-shell double emulsions have a number of advantages, including high loading capacity, improved stability and usability as templates for producing various materials (capsules, colloidalsomes, polymersomes and liposomes). However, previous studies mainly focused on using ultrathin-shell double emulsions as templates for preparing other materials, and the process always involves toxic solvents (e.g. chloroform) to dissolve polymers or lipids followed by raising the temperature to evaporate the solvent.[6,7] This might be detrimental to temperature-sensitive drugs or biological components encapsulated

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in the double emulsions. Also, the residual toxic solvents in the materials may also have negative effects on their biomedical or food applications. Therefore, it is important to make stable double emulsions. To the best of our knowledge, the controlled generation and stability of ultrathin-shell double emulsions have not yet been widely studied.

We previously reported the generation of ultrathin-shell double emulsions using viscous fish oil as the middle phase, and their stability was significantly improved.[8] However, the fundamental understanding about which kinds of systems are able to form stable double emulsions and the effect of different parameters on the formation of ultrathin double emulsions remains unclear. In this work, we investigated different parameters that control the formation of ultrathin-shell double emulsions, including the density and viscosity of the middle phase and the interfacial tensions, and optimised the system and operation conditions for the formation of ultrathin-shell double emulsions. We fabricated different sizes of monodisperse double emulsions in the dripping regime and showed that ultrathin-shell double emulsions are stable for a long period of time, and this makes this new approach suitable for various microencapsulation applications.

## 2. Results and Discussion

### 2.1. Formation of Thin-Shell Double Emulsions

The glass capillary device used to make ultrathin-shell double emulsions is schematically shown in Figure 1. Three inlets (inlets 1–3) are used to introduce the inner, middle and continuous phases, respectively, and the outlet is used to collect the product. In this work, we focused on W/O/W double emulsions

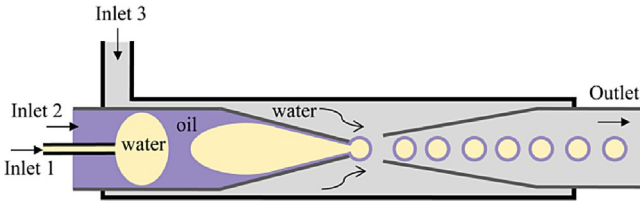


**Figure 1.** Schematic illustration of the glass capillary device used to make ultrathin-shell double emulsions. Inlet 1: the inner phase, inlet 2: the middle phase and inlet 3: the continuous phase.

and used a 10 wt% aqueous solution of poly(vinyl alcohol) (PVA) as the inner and outer continuous phases. The inner aqueous phase is introduced at inlet 1 and breaks into big droplets, which are dispersed in the middle oil phase (inlet 2). The inner wall of the glass capillary is modified to be hydrophobic, so the oil phase wets the surface. When the big water droplets travel to the tip, the oil phase is squeezed into a thin film, which wraps around the inner phase. Then the biphasic stream of inner aqueous phase and the middle oil phase enters the continuous aqueous flow, and a spherical bulb forms at the tip of the tapered capillary. Different from the formation of single emulsions, the bulb containing a water core and an oil shell may burst before it forms a double emulsion. As the inner phase is the same as the outer phase (both are aqueous phases), they have the same contrast, but the middle oil phase has pronounced contrast with the inner and outer aqueous phases and appears dark (Figure 2a), whereas the ultrathin-shell double emulsions only show a dark outline (Figure 2c).

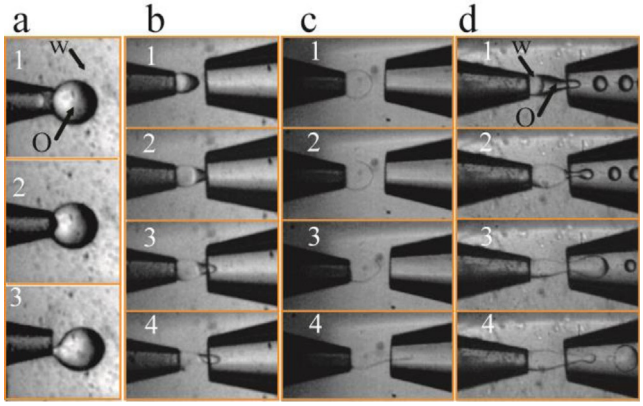


**Figure 2.** Formation of thin-shell double emulsions. Different middle oil phases were used to test the effect of surfactant in the oil phase. a) 10% PVA/hexane/10% PVA (convention: inner phase/middle phase/outer phase), b) 10% PVA/hexadecane/10% PVA, c) 10% PVA/hexadecane containing 1% Span 80/10% PVA and d) 10% PVA/hexadecane containing 2% Span 80/10% PVA. a), b) No double emulsion was formed when the surfactant was absent from the middle phase. c) Double emulsions were only formed in the jetting regime when 1% Span 80 was added to in the oil phase. d) With increasing concentration of the surfactant in the oil phase, double emulsions were formed in the dripping regime.

Generally, four different cases were observed depending on the property of the middle oil phase, as shown in Figure 2. When pure hexane was used as the middle phase (Figure 2a), an oil bulb was first formed at the tip, followed by the water droplet growing inside the bulb. When the inner water droplet became too big, it broke through the oil layer with formation of single oil droplets. A slightly different scenario was observed when the middle phase was hexadecane. A thin layer of oil wrapping the inner water phase was formed, and it burst before a neck formed (Figure 2b). When a small amount of surfactant (1 wt% Span 80) was added to hexadecane, ultrathin-shell double emulsions were formed, but only in the jetting regime under certain flow conditions. We further increased the concentration of Span 80 to 2 wt%, and a stable biphasic flow was formed, followed by the formation of a neck and the breakup of the ultrathin-shell double emulsions (Figure 2d).

To systematically investigate the parameters of the middle oil phase that affect the formation of ultrathin-shell double emulsions, we tested and compared different systems, as summarized in Table 1. Double emulsions were not generated when pure solvent was used as the middle phase, and the result was independent of the density and viscosity of the middle phase. In the presence of surfactant (Span 80) in the middle oil phase at a low concentration of 1%, the systems were able to form thin-shell double emulsions only at certain

**Table 1.** Effects of various parameters on the formation of double emulsions.

| Parameter | Inner (1) | Middle (2) | Outer (3) | Double emulsion? |
|---|---|---|---|---|
| density of the middle phase | 10% PVA | hexane ($\rho = 0.655$ g mL$^{-1}$) | 10% PVA | no |
| | 10% PVA | hexadecane ($\rho = 0.77$ g mL$^{-1}$) | 10% PVA | no |
| | 10% PVA | 36% chloroform and 64% hexane ($\rho = 0.952$ g mL$^{-1}$) | 10% PVA | no |
| viscosity of the middle phase | 10% PVA | hexane ($\mu = 0.3$ MPa s) | 10% PVA | no |
| | 10% PVA | hexadecane ($\mu = 3.474$ MPa s) | 10% PVA | no |
| Interfacial tension | 10% PVA | hexane + 1% Span 80 | 10% PVA | yes[a] |
| | 10% PVA | hexadecane + 1% Span 80 | 10% PVA | yes[a] |
| | 10% PVA | hexadecane + 2% Span 80 | 10% PVA | yes |
| | 10% PVA | hexadecane + 5% Span 80 | 10% PVA | yes |

[a] At certain flow rates.

flow rates in the jetting regime, which agrees with a previous study by Kim et al.,[6] as shown in Figure 2c. When the concentration of Span 80 was increased to 2%, double emulsions could be generated in both the jetting and dripping regimes, as shown in Figure 3. The flow rate of the outer phase was kept at 4000 μL h$^{-1}$. At low flow rates of both the inner and middle phases, double emulsions were formed in the dripping regime (circles in Figure 3a and an example in Figure 3b1). In this regime, droplets break up at the tip of the glass capillary, forming monodisperse double emulsions. There were two cases in which the system shifted to jetting.[9] In the first case, the flow rate of the middle phase increased, and the shear stress on the droplet was large enough to overcome the interfacial tension and led to jetting. In the second case, the flow rate of the inner phase increased, and the inertial force was large enough to overcome the interfacial tension and resulted in jetting, as shown in Figure 3b2. These results suggest that the presence of surfactant in the middle oil phase, which lowers the interfacial tension, is crucial to make thin-shell double emulsions, and that the operating regime depends on the flow rates of the inner and middle phases. In the following study, double emulsions were produced in the dripping mode. This regime generates single oil droplets and ultrathin-shell double emulsions intermittently. Separation of the double emulsion from the single oil droplets can be achieved by their density difference, as single oil droplets are much lighter.

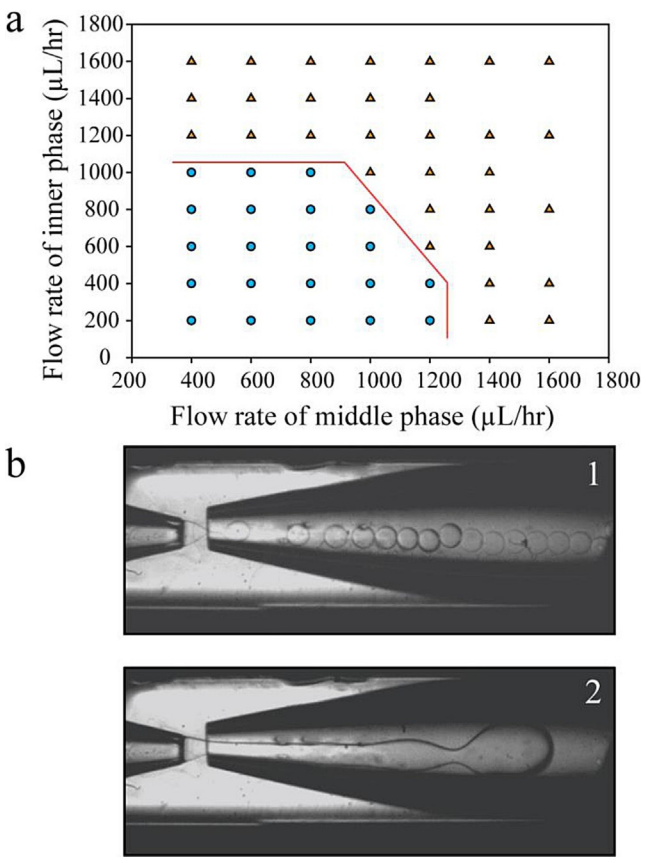


**Figure 3.** Dependence of the jetting and dripping regimes on the flow rates of the inner and middle phases. a) Regime of double-emulsion formation as a function of the flow rates of middle and inner phases. The flow rate of the continuous phase was maintained at 4000 μL h$^{-1}$. Circles and triangles denote stable dripping regime and unstable jetting regime, respectively. b) Formation of double emulsions in the dripping regime (1) and jetting regime (2). The three-phase system was 10% PVA/hexadecane with 2% Span 80/10% PVA.

To further elucidate the role of surfactant, interfacial tensions of the inner and outer interfaces were measured and compared (Figure 4). The interfacial tension of an oil droplet dispersed in an aqueous phase (O/W interface), representing the interface between the middle oil and outer water phases, is shown in Figure 4a. Though an aqueous solution with a high concentration of PVA (10 wt%) was used as the outer phase, the interfacial tension was high (52 mN m$^{-1}$), and was very close to that between hexadecane and pure water (53 mN m$^{-1}$); this was attributed to the slow adsorption of PVA onto the interface. The interfacial tension then slowly decreased to an equilibrium value of 37 mN m$^{-1}$. Therefore, when the O/W interface formed, there was not enough surfactant on the interface and the outer O/W interface was unable to encapsulate the inner droplet due to its high tension, as observed in Figures 2a and b. In contrast, the interfacial tension of 10% PVA in hexadecane started from 17 mN m$^{-1}$ and dropped to approximately 13 mN m$^{-1}$. In the presence of a low concentration of surfactant (1 wt% Span 80), the interfacial tension was substantially reduced, but not low enough to keep the interface stable. As a result, double emulsions can only be produced in the jetting regime at certain flow rates. When the concentration of Span 80 is increased to 2 wt% or even higher, the interfacial tensions of both the inner W/O and outer O/W interfaces are very low. Therefore, interfacial tension plays an important role in producing thin-shell double emulsions and can be controlled by adding surfactants to the middle, oil phase.

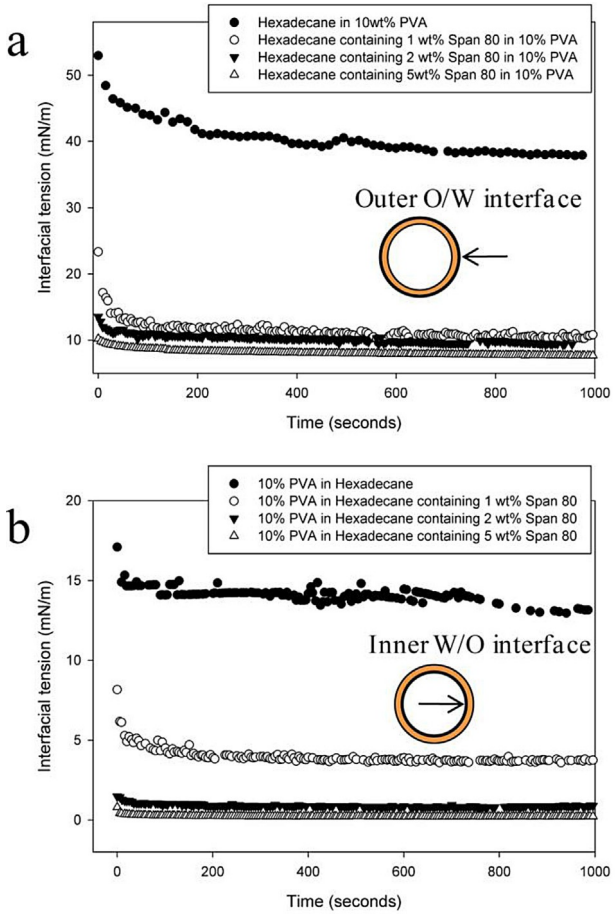


**Figure 4.** Profiles of dynamic interfacial tension. a) The interfacial tension between the middle and outer phases: hexadecane containing different concentrations of Span 80 in 10% PVA. b) The interfacial tension between the inner and middle phases: 10% PVA in hexadecane containing 1, 2 and 5% of Span 80.

### 2.2. Effect of Flow Rates on the Size and Shell Thickness of Double Emulsions

To produce monodisperse thin-shell double emulsions, the system was operated in the dripping regime. In this regime, the formation of double emulsions is dominated by two competing forces: the shear force that drags the drop and the capillary force that holds the drop to the tip. The relative ratio of shear force to capillary force is usually expressed as the capillary number *Ca*, one of the most important parameters in microfluidics [Eq. (1)]:[10]

$$Ca = \frac{\mu \cdot u}{\sigma} \quad (1)$$

where $\mu$ is the dynamic viscosity [Pa s], $u$ the characteristic velocity of the continuous phase [m s$^{-1}$] and $\sigma$ the interfacial tension [N m$^{-1}$]. Therefore, we can control the size of the double emulsions by tuning the flow rate of the outer phase (shear force) or the interfacial tension (capillary force). Figure 5a and b show that when the flow rate of the continuous phase increases, the size of the double emulsions decreases. If we keep the flow rates the same, the size decreases with increasing concentration of the surfactant (Figure 5c), that is, the lower the interfacial tension the smaller the droplet size. In contrast, the size of double emulsions is independent of the flow rates of the inner and middle phases. We calculated the capillary number for our systems using $\mu = 10$ MPa s and $\sigma = 23.3$, 16 and 10.22 mN m$^{-1}$ for the three systems with different concentrations of Span 80 (1, 2 and 5%). The interfacial tension data we used here are the starting point (0 s for Figure 4a), because the dynamic interfacial tension matters more than the equilibrium interfacial tension, since droplet formation normally takes place on a timescale of tens of milliseconds. At the lower surfactant concentrations (1 and 2% Span 80), the starting interfacial tensions are much higher than the equilibrium values. The dependences of the emulsion size on the outer flow rate and the interfacial tension indicate an inverse correlation between the size and the capillary number [Figure 5d and Eq. (2)]:

$$d \propto \frac{1}{Ca} \quad (2)$$

which is analogous to the behaviour of single-emulsion formation in co-flows and T-junctions.[11] This validates the effects of shear force and capillary force on the size of ultrathin-shell double emulsions.

The shell thickness $L$ of the double emulsion was calculated by using the method reported in the literature.[6] The rupture of a W/O/W double emulsion results in a single O/W droplet. The volume of the single O/W droplet is equal to the volume of oil in the shell of the double emulsion. Therefore, the relation between the size of double emulsion drops $R_d$, the size of the resulted single emulsion drops $R_s$ and the shell thickness $L$ is [Eq. (3)]:

$$\frac{4}{3}R_d^3 = \frac{4}{3}R_s^3 + \frac{4}{3}(R_d - L)^3 \quad (3)$$

that is, [Eq. (4)]:

$$L = R_d - (R_d^3 - R_s^3)^{1/3} \quad (4)$$

For double emulsions generated from the system of 10% PVA/hexadecane with 2% Span 80/10% PVA at flow rates of 800/400/4000 μL h$^{-1}$, the size of double emulsions is approximately 202 μm and the size of the oil drop is around 37 μm, as shown in Figure 5e. From Equation (4), the shell thickness $L$ is about 208 nm, which is much smaller than that of double emulsions made by other methods. In this discontinuous dripping regime, the shell thickness is independent of the flow rates and remains around 200 nm. This is mainly because most of the oil phase forms single oil droplets, and only a small volume of oil is used for forming the ultrathin-shell double emulsions.[6]

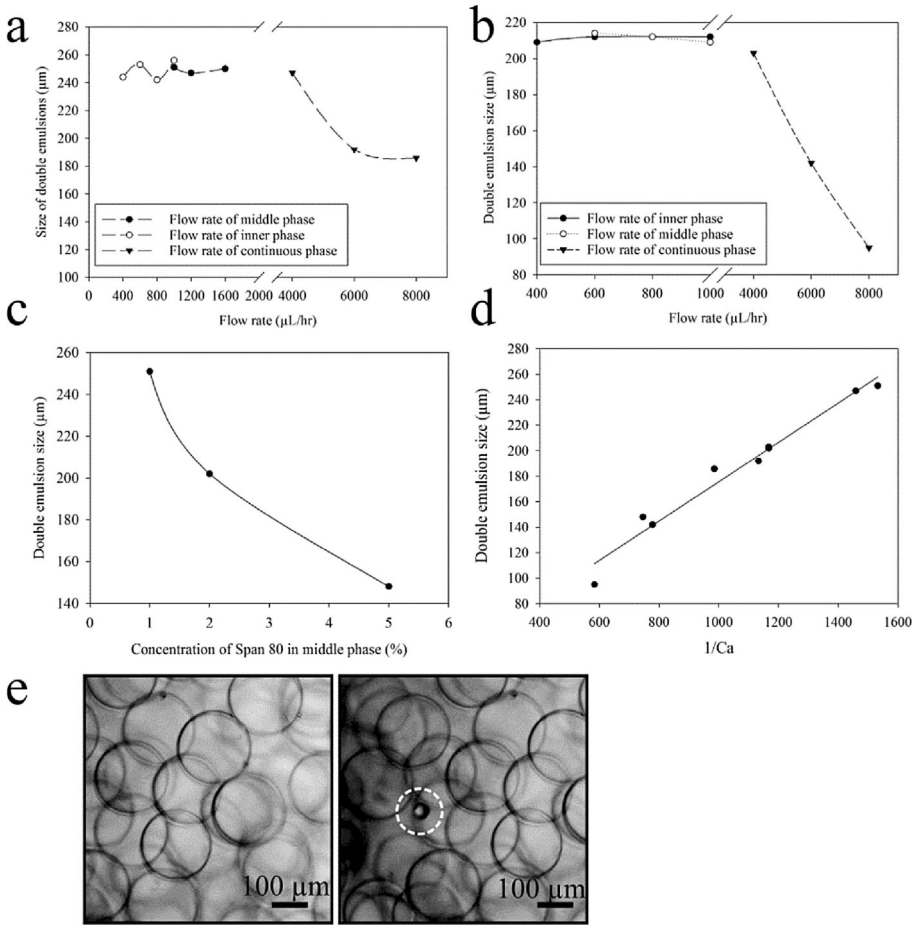


**Figure 5.** Size control of ultrathin-shell double emulsions. a) Size dependence of the double emulsions with 1% Span 80 in hexadecane. The size is independent of the flow rate of the inner (flow rates of the middle and outer phases fixed at 2000 and 4000 μL h$^{-1}$, respectively) and middle phases (flow rates of the inner and outer phases fixed at 400 and 4000 μL h$^{-1}$, respectively). The size decreases with increasing flow rate of the outer phase (flow rates of the inner and middle phases fixed at 400 and 1600 μL h$^{-1}$, respectively). b) A similar trend is observed in double emulsions with 2% Span 80 in hexadecane. Flow rate of inner phase: the middle- and outer-phase flow rates were 800 and 4000 μL h$^{-1}$, respectively. Flow rate of middle phase: the inner- and outer-phase flow rates were 600 and 4000 μL h$^{-1}$, respectively. Flow rate of continuous phase: the inner- and middle-phase flow rates were 400 μL h$^{-1}$ and 400 μL h$^{-1}$, respectively. c) Effect of surfactant concentration on the size (flow rates were fixed at 400/1000/4000 μL h$^{-1}$). d) Correlation between the size of double emulsions and *Ca*. e) Optical images of ultrathin-shell double emulsions. Rupture of a double emulsion results in a small oil droplet, as highlighted by the dotted circle.

### 2.3. Stability of Thin-Shell Double Emulsions

Generally, macroemulsions with a diameter greater than 0.1 μm are not thermodynamically stable and are only kinetically metastable, as they undergo breakage or coalescence over time, which is driven by the Laplace pressure or density mismatch.[5b,12] However, the current ultrathin-shell double emulsions are stable for a long period of time. The system of 10% PVA/hexadecane/10% PVA was systematically studied to explore different parameters that affect the stability of double emulsions. In the absence of surfactant in the middle oil phase, no double emulsion can be made. When a small amount of surfactant is added to hexadecane, thin-shell double emulsions can be produced in the jetting regime at certain flow rates; however, they are unstable due to the high interfacial tension of the inner W/O interface. After 1 h, all these double emulsions broke (Figure 6a). When the concentration of Span 80 was increased to 2% or even 5%, double emulsions could be produced at a broad range of flow rates, and they remained stable for more than ten weeks. The structure of the thin-shell double emulsions remained intact, as observed by microscopy (Figure 6b).

We have thus demonstrated that ultrathin-shell double emulsions can be stable for an extended time. The presence of surfactant (Span 80) in the middle oil (hexadecane) phase plays an important role in stabilizing the double emulsions. By considering the inner W/O and outer O/W interfaces separately, it is easy to understand that the presence of PVA in the outer aqueous phase stabilises the outer O/W interface, while Span 80 in the middle oil phase is responsible for the stability of the inner W/O interface. However, selection of surfactants that match the middle oil phase is also important. We tested some other systems with different oils as the middle phase, and we found that no double emulsions could be generated when olive oil or fish oil containing Span 80 was used at the middle oil phase,[8] because the interfacial tension is extremely low (e.g., 0.8 mN m$^{-1}$ for fish oil containing 2 wt% Span 80 in 10 wt% PVA). Such low interfacial tension resulted in an unsta-

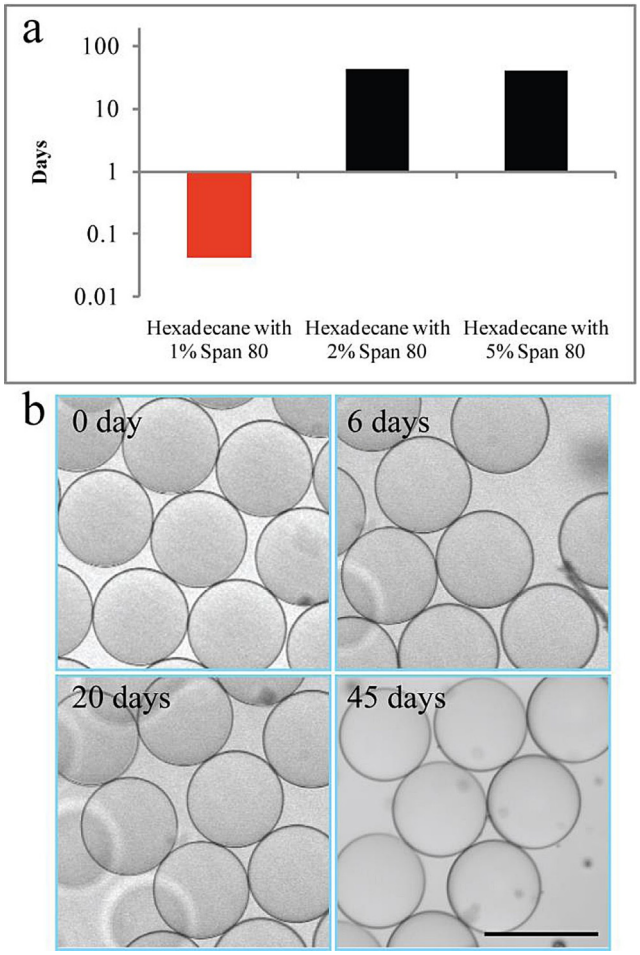


**Figure 6.** Stability of ultrathin-shell double emulsions. a) Double emulsions containing 2% or more surfactant in the middle oil phase show long-term stability. b) Optical images of the double emulsions over time (hexane with 2% Span 80). The scale bar is 200 μm.

ble jetting regime, whereas the other surfactant, ABIL EM 90, gives an interfacial tension of 5 mN m$^{-1}$, which is capable of forming double emulsions. Therefore, different surfactant may be required for different oil phases to make and stabilize ultrathin-shell double emulsions.

## 3. Conclusions

We explored the formation and stability of W/O/W ultrathin-shell double emulsions. We showed that for systems of 10% PVA/hexadecane/10% PVA, the presence of surfactant Span 80 in the middle oil phase facilitates the formation of double emulsions and stabilizes the core–shell structures. Both dripping and jetting regimes were observed, depending on the flow rates of the inner and middle phases. In the dripping regime, the size of double emulsions was independent of the flow rates of the inner and middle phases, but decreased as the flow rate of the outer phase increased. The decrease in interfacial tension also made the double emulsions smaller, with an inverse relation between the droplet size and the capillary number. The stability of thin-shell double emulsions can be significantly improved by increasing the concentration of Span 80 in the middle oil phase, and they were stable up to more than ten weeks. This study provides an example of stable double emulsions and paves the way for their future applications in various fields, such as foods, cosmetics, pharmaceuticals and so forth.

## Experimental Section

A 10 wt% aqueous solution of PVA ($M_w$ = 13 000–23 000) was used as the continuous and inner phases. A number of solvents were used as the middle phase, including hexane, hexadecane and chloroform/hexane (36:64, v/v). Different concentrations of Span 0 (1, 2 and 5 wt%) were dissolved in the middle phase to reduce interfacial tension. A 100 mM aqueous solution of sucrose (VWR) was prepared to collect the emulsion droplets.

Glass microcapillary devices used in this work were fabricated by a standard procedure published previously.[6–8] Briefly, two circular capillaries (ID 0.58 mm, OD 1.00 mm) were tapered to 20 μm with a P-97 micropipette puller (Sutter Instrument, Inc.) and sanded to 100 and 200 μm in diameter. The capillary with the tapered end of 100 μm was surface-modified with *n*-octadecyltrimethoxysilane to make it hydrophobic, and the other (200 μm) was treated with 2-[methoxy(polyethyleneoxy)propyl]trimethoxysilane to make it hydrophilic. We then stretched a third cylindrical capillary to make it thinner (OD 150 μm). We assembled the device by inserting the two tapered capillaries into the two ends of a square capillary (ID 1.05 mm) with the smaller one on the left. They were then aligned to maintain a separation of about 100 μm. Then the stretched capillary was inserted into the left capillary. Finally, dispensing needles were placed and fixed.

The inner, middle and outer phases were filled into 5, 5 and 30 mL plastic syringes (BD), respectively. The needles of the syringes were connected with the dispensing needles of the microcapillary device by using polyethylene tubing of inner diameter 0.86 mm (Scientific Commodities, Inc.). Harvard pumps (Harvard Apparatus) were used to pump the liquid phases at constant flow rates. Different combinations of flow rates were investigated for different systems to form ultrathin-shell double emulsions. For stability studies, 3 mL of single or double emulsions was collected in 100 mM sucrose solutions.

The production of double emulsions in microcapillary devices was recorded with a high speed camera (Phantom V7.3). The double-emulsion droplets were observed by bright-field microscopy (Leica).

A Krüss Drop Shape Analysis System DSA10 (Krüss GmbH, Hamburg, Germany) was used to measure interfacial tensions. For oil-in-water systems, the water phase was filled into an 8 mL quartz cuvette, and an oil droplet was generated from a U-shaped needle if the density of the oil phase was lower than that of the aqueous phase, and otherwise by using a straight needle. The dynamic interfacial tension was measured by analysing the droplet shape every 2 s over a period of 1000 s.

## *Acknowledgements*

*C.X.Z. acknowledges financial support from Australian Research Council through the award of a 2014 ARC Future Fellowship (FT140100726). The work was supported by the National Science*

*Foundation (DMR-1310266) and the Harvard Materials Research Science and Engineering Centre (DMR-1420570).*

## Conflict of interest

*The authors declare no conflict of interest.*

**Keywords:** glass capillary devices · emulsions · encapsulation · interfaces · microfluidics

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Manuscript received: December 1, 2016
Accepted Article published: January 23, 2017
Final Article published: March 20, 2017