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ARTICLE

Controlled coalescence of two immiscible droplets for Janus emulsions in a microfluidic device

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We developed a simple microfluidic device to prepare Janus emulsions by controlled coalescing of two immiscible drops. We could prepare Janus emulsions with different size and structures by changing three phase flow rates and the concentration of additives in different phases, and control the equilibrium contact angle θ_{AB} in the range of 120°~190°. Furthermore, we firstly found that the coalescence process of two immiscible droplets would be quicker when the equilibrium structure of Janus emulsion tends to be 'complete engulfing'. The results will be helpful for preparing Janus emulsions with controlled structures in microfluidic device.

Introduction

Multiple emulsions such as O/W/O double emulsions [1], G/W/O double emulsions[2], and Janus emulsions[3], have been widely used in the fields of bio-medicine[4, 5], food science [6, 7] and cosmetics[8]. Janus emulsion has attracted considerable attention because of its unique anisotropy properties. According to the previous study[9], the equilibrium structure of three phase fluids is determined by three interfacial tensions. Defining the two immiscible dispersed phases as phase 1 and phase 2, the continuous phase as phase 3, we can determine the emulsion structure of equilibrium by the relationship between different interfacial tensions σ_{ij} ($i \neq j \neq k=1,2,3$) .

Researchers defined the spreading coefficients S to judge the structure of equilibrium based on Interfacial Energy Minimization Principle[9]

$$S_i = \sigma_{jk} - (\sigma_{ij} + \sigma_{ik}) \qquad (1)$$

When the spreading coefficients S is more or less than 0, there are three different equilibrium conditions that will be: (I) complete engulfing, (II) partial engulfing (Janus) and (III) non-engulfing. Among them, Janus structure can be formed only if all three spreading coefficients are less than 0.

Traditional method of preparing Janus emulsions is agitation. Hasinovic et al.[3] obtained water-vegetable oil Janus emulsions in silicone oil by using the Mini Vortexer mixed the samples. Ge et al.[10] mixed certain weight fractions of silicone oil (SO), tripropyleneglycol diacrylate (TPGDA) and Tween 80 aqueous solution with the Ultra-Turrax , then attained the Janus emulsions of TPGDA/SO in water. While the traditional agitation method to prepare Janus emulsions has many disadvantages, such as poor monodispersity of the Janus emulsions, difficulties to control structure and repeat the product.

Microfluidic technology[11-17] has enabled the formation of complex multiple emulsions with good monodispersity, controlled structures and droplet size in microchannels, which solves the problems of traditional method. So microfluidic technology becomes the promising method to prepare Janus emulsions in the past decade. Typical approaches to prepare Janus emulsions in microfluidic devices are dewetting, laminar shear-rupturing and phase separation.

Nie et al. [11] used hydraulics focusing microchannels to prepare double emulsions and Janus emulsions. When the three liquid fluids flowed into a narrow orifice, the continuous water phase surrounded the monomer-oil thread. The coaxial jet extended into the downstream channel and broke up into core-shell double emulsions. For some systems, the emulsions would dewetting to form Janus emulsion with the thermodynamic properties. Xu et al. [12, 13] used the co-flowing coaxial microfluidic device to prepare double emulsions with different cores. Then the inner phase broke out because of their thermodynamic properties and the emulsion formed Janus structure. They investigated the structure evolution of the double emulsions for different systems. These methods are called as dewetting approaches.

Nisisako et al.[14] firstly used a laminar microfluidic system to produce biphasic Janus droplets. They chose 1,6-hexanediol diacrylate (HDDA) and silicone oil as dispersed phase fluids, and sodium dodecyl sulfate (SDS) 0.3 wt.% aqueous phase as continuous phase fluid. Then they prepared biphasic Janus droplets of two immiscible organic fluids by a shear-rupturing method. Lan et al.[15] chose the same systems in a coaxial microfluidic device. As the dispersed phase flowed through the shrink tip of the glass capillary, monodispersed Janus droplets were produced by the shearing force of the continuous phase flow. Then the Janus droplets were photopolymerized by exposing to the UV light. Based on the mechanism of shear-force-driven break-off, Prasadet al.[16] also

prepared shape-controlled Janus droplets and successfully synthesized monodispersed inorganic-organic Janus microparticles. Ono et al.[17] prepared Janus particles by using a phase separation method. They prepared droplets of polymer molecules (PS and PMMA) that were dissolved in the polar solvent at concentration of 1.0-5.0 % (w/v) firstly using hydraulics focusing microchannels. The external phase fluid was distilled water containing 2.5% (w/v) PVA. Then the solvent in the droplets were rapidly diffused and dissolved into the continuous phase during flowing process, whereas water-insoluble polymers were precipitated to form monodispersed polymeric Janus microparticles.

However, there are many problems about the existing approaches to prepare Janus emulsions in microfluidic devices, such as complex fabrication of microfluidic devices, high requests to control flow and narrow operation range. So it is desirable to develop a simple and convenient approach to prepare Janus emulsions with controlled structures in microfluidic devices.

Learning from the coalescence of two droplets with same phase, we develop a new microfluidic approach to prepare Janus emulsions by coalescing two immiscible drops combined with changing interfacial tensions. During the coalescing of two same phase droplets, there are three distinct stages [18]: approach and deformation by collision, lubricating film drainage, and coalescence by rupture of the film. When the contact time of droplets is longer than the film drainage time, the coalescence occurs. On the contrary, the two droplets will never coalesce[19]. While for the coalescing two immiscible drops, after lubricating film drainage and the film rupturing, one droplet will partly spread on the surface of another droplet and form Janus structure. To the best of our knowledge, the spreading process and thermodynamic principle during the coalescence of two immiscible drops has not been studied. So we changed the experimental systems and systematically investigated the influences of interfacial tensions on the spreading dynamics and thermodynamic equilibrium structures of Janus emulsions.

Materials and methods

The microfluidic device was fabricated on a polymethyl methacrylate (PMMA) plate using a Computerized Numerical Control (CNC) machine tool with an end mill (Φ=0.4 mm), as shown in Fig. 1. The width and the depth of microchannels are both 400μm. Two dispersed phase fluid flows (red and yellow fluids in the figure) are driven into the microchannel from both sides separately through two microneedles with inside diameter of 160 μm, then sheared by continuous phase fluids (blue fluids) to form monodispersed droplets. Then, the droplets of two dispersed phase meet at the subsequent T junction, and flow into an expanded chamber where two immiscible droplets tend to collide and coalesce. The size of expanded chamber is 6.0 mm (length) ×2.4 mm (width) ×0.4 mm (depth).
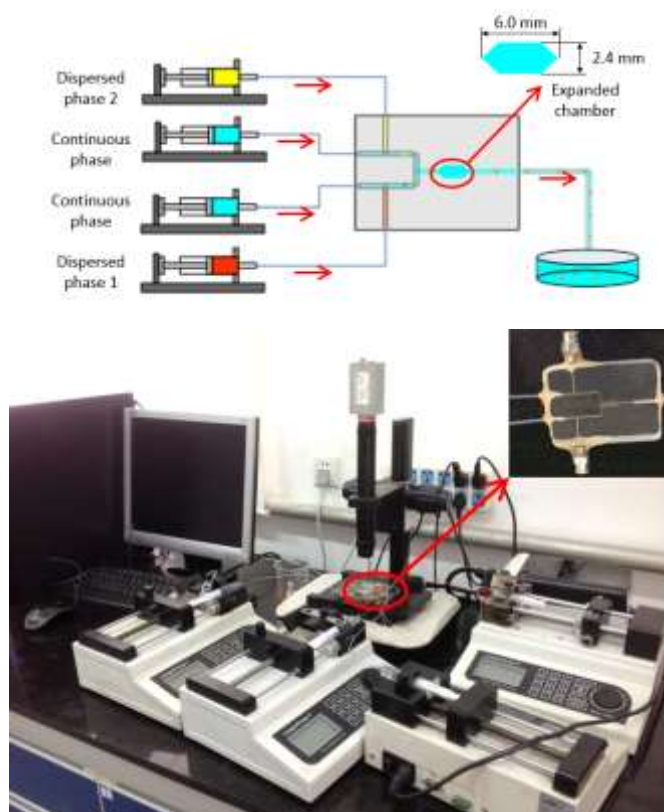

Figure 1. The structure of the microfluidic device and snapshot.

To prepare Janus emulsions, we chose soybean oil (Yihai Kerry Food Company) and deionic water as dispersed phases, silicone oil (10cs, XIAMETER) as continuous phase. Based on the previous results [20-22], to vary interfacial tensions, we added 1.5 wt.% PGPR (Polyglycerol Polyricinoleate) and 0-40 vol.% 1-octanol (Tianjin Yongda Chemical Reagent Company Limited) into soybean oil, and dyed soybean oil by Sudan III (Tianjin Fuchen Chemical Reagents Factory). 0-1.0 wt.% SDS (Tianjin Fuchen Chemical Reagents Factory) was added into water, and 0-10 wt.% Dow-Corning 749 (Dow Corning Co. Ltd.) was added into silicone oil.

We observed the formation and coalescence processes of emulsions in microchannel by an optical microscope (Olympus, Japan) equipped with a camera (A742, Pixelink, Canada) which frequency is 200 images per second. The interfacial tensions were measured by an interfacial tension meter using the pendant drop technique (OCAH200, GmbH, Germany). All the experiments were carried out at room temperature.

Results and discussion

Preparation of Janus emulsions by coalescence method

Firstly, we attempted to prepare Janus emulsions of two different structure controllably. We added 1.5 wt. % PGPR into soybean oil (52.8 mPa s) and 0.5 wt.% Dow-Corning 749 (DC 749) into the silicone oil (9.67 mPa s). When a soybean oil drop meets a water (0.95 mPa s) drop at the expanded chamber, the soybean oil drop will spread out on the surface of water drop partly and forms a

typical Janus emulsion. By changing the phase flow rates of dispersed phases and continuous phase, we successfully prepare typical Janus emulsions with different volume ratio of soybean oil drop to water drop in the range of 0.5~2. We could also prepare Janus emulsions with the number of water drop to soybean oil drop ratio is 1:1 or 1:2 separately. The micrographs of different Janus emulsion are shown in Fig. 2. And the videos showing the generation of different Janus emulsions can be seen in the Supporting Information (Movies S1 ~ S4).

(a) DP1: 0.5   DP2: 1.6   CP1: 22.0   CP2: 30.0

(b) DP1: 2.5   DP2: 1.6   CP1: 21.0   CP2: 30.0

(c) DP1: 3.0   DP2: 1.4   CP1: 17.0   CP2: 30.0

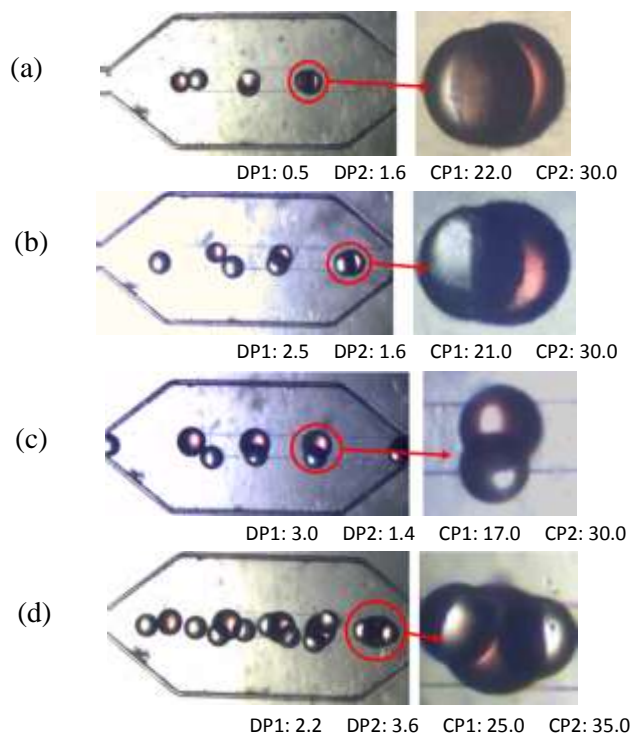(d) DP1: 2.2   DP2: 3.6   CP1: 25.0   CP2: 35.0

Figure 2. Preparation of typical Janus emulsions with different structures. (a-c) Structure of typical Janus emulsions with volume ratio as 1:1, 1:2 and 2:1; (d) Structure of typical Janus emulsions of two water droplet to one soybean oil droplet. DP1 and DP2 are the flow rates of dispersed phase 1 and dispersed phase 2 respectively. CP1 and CP2 are flow rates of continuous phase from the side of dispersed phase 1 and dispersed phase 2 respectively. The units of flow rate are μL min^{-1}.

Table 1 The interfacial tensions and spreading coefficients of typical Janus emulsions.

Phase 1	Soybean oil with 1.5 wt.% PGPR	σ_{12}/mN m^{-1}	11.24	S_1	-1.76
Phase 2	Water	σ_{13}/mN m^{-1}	3.28	S_2	-20.72
Phase 3	Silicone oil with 0.5 wt.% DC 749	σ_{23}/mN m^{-1}	12.76	S_3	-4.80

Then we changed the experimental system by adding 1.0 wt.% SDS into water phase (0.99 mPa s). We found obvious differences on the structure of Janus emulsions. The soybean oil drop almost engulfed the water drop, as shown in Fig. 3. We successfully prepared approximate-engulfed Janus emulsions with different structures by changing the dispersed phases and continuous phase

flow rates. And the videos showing the generation of different Janus emulsions can be seen in the Supporting Information (Movies S5 & S6).

(a) DP1: 1.6   DP2: 1.5   CP1: 21.0   CP2: 13.0

(b) DP1: 1.6   DP2: 3.0   CP1: 21.0   CP2: 13.0

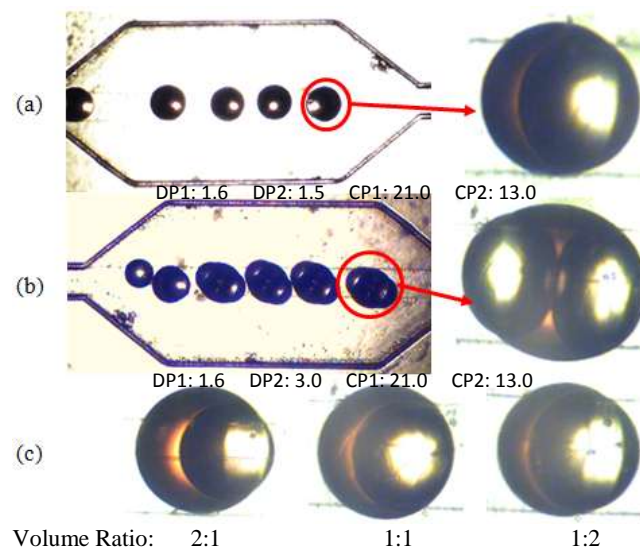(c) Volume Ratio: 2:1   1:1   1:2

Figure 3. Preparation of approximate-engulfed Janus emulsions with different structures. (a) Structure of approximate-engulfed Janus emulsions; (b) Structure of approximate-engulfed Janus emulsions of two water droplet to one soybean oil droplet; (c) Structure of approximate-engulfed Janus emulsions with volume ratio as 2:1, 1:1 and 1:2. DP1 and DP2 are the flow rates of dispersed phase 1 and dispersed phase 2 respectively. CP1 and CP2 are flow rates of continuous phase from the side of dispersed phase 1 and dispersed phase 2 respectively. The units of flow rate are μL min^{-1}.

Table 2 The interfacial tensions and spreading coefficients of approximate-engulfed Janus emulsions.

Phase 1	Soybean oil with 1.5 wt.% PGPR	σ_{12}/mN m^{-1}	4.27	S_1	0
Phase 2	Water with 1 wt.% SDS	σ_{13}/mN m^{-1}	3.28	S_2	-8.65
Phase 3	Silicone oil with 0.5 wt.% DC 749	σ_{23}/mN m^{-1}	7.66	S_3	-6.67

We calculated the spreading coefficients using Eq.1 in Table 1 and 2. According to the spreading coefficients of the systems in Table 1 and 2, we predicted the three phases would form Janus structure and a structure between Janus and engulfing respectively. And the experimental results of the equilibrium structures matched the predictions well.

From above results, we successfully prepared Janus emulsions by coalescing of two immiscible droplets method, and we could control the structure and size of Janus emulsions by changing the experimental systems and flow rates of continuous phase and two dispersed phase fluids. The experiments we did proved that it is feasible to prepare Janus emulsions by coalescing method in microfluidic device. To the best of our knowledge, the spreading process and thermodynamic principle during the coalescence of two immiscible drops has not been studied. So we changed the experimental systems and systematically investigated the influences

of interfacial tensions on the coalescing dynamics and thermodynamic equilibrium structures in the following section.

The coalescence dynamics and the control of Janus emulsion equilibrium structures

From the references [23-25], we can define three contact angles of a Janus emulsion droplet, as shown in Fig. 4. The interfacial tension between phase A/B and external phase is γ_A/γ_B whose direction is depicted in Fig. 4. γ_{AB} is the interfacial tension between phase A and phase B. From the force balance between these three interfacial tensions, three contact angles of θ_A, θ_B and θ_{AB} for the equilibrium Janus emulsion droplet can be determined. The angle between γ_A and γ_B is θ_{AB} that indicates the engulfing extent of two immiscible drops. The smaller θ_{AB} is, the more separated the two immiscible drops are. On the contrary, the bigger θ_{AB} is, the more one drop engulfs another.
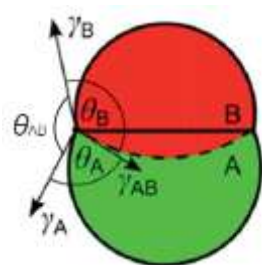
Figure 4. The sketch of three contact angles of Janus emulsion droplet

From the above analysis we can see that interfacial tensions between any two phases affect Janus emulsion structure greatly. As the surfactant in water phase, SDS decreases the interfacial tensions between water phase and other phases. So does DC 749 in silicone oil. And from references [20] we learned that adding octanol into soybean oil decreases the interfacial tensions between soybean oil phase and other phases. So we changed the concentration of additive in one phase with the other phases staying the same to investigate the effect of additive concentration on the coalescence dynamics and equilibrium structure of Janus emulsions. In the following experiments, we fixed the flow rates of dispersed phase 1 and dispersed phase 2 both as about 1μL min^{-1}, and flow rates of continuous phase from the side of dispersed phase 1 and dispersed phase 2 as about 20μL min^{-1} and 25μL min^{-1} respectively.

Firstly, we fixed deionized water as phase B and silicone oil that contained 0.5 wt.% DC 749 as external phase, and changed phase A as soybean oil containing 1.5 wt.% PGPR with different concentration of octanol. The typical dynamic process of coalescence is shown in Fig. 5a. When two immiscible droplets contacted, we started the time. And two droplet maintained the contact state for a while. Then one droplet began to engulf another and reached equilibrium at the end, we ended the timer at this time. The time record was coalescence time. We repeated recorded each experiment for ten times and get the average coalescence time. We recorded a lot of videos, selected that very moment that the interface between phase A and phase B in Janus emulsion was perpendicular to the plane of microchannels, and measured the contact angle

correctly. When the octanol concentration in phase A increased from 0 to 25 vol.%, we found the interfacial tensions γ_A decreased from 1.12 mN m^{-1} to 0.63 mN m^{-1}, and γ_{AB} decreased from 23.17 mN m^{-1} to 11.08 mN m^{-1} as shown in Table 3. We can see that the interface between phase A and phase B tended to be smaller than that between phase A and external phase. So the water drop was engulfed more by the soybean oil drop gradually to reach smallest Interfacial Energy, and the contact angle θ_{AB} of Janus emulsion droplet increased, as shown in Fig. 5b. Furthermore, the effect of θ_{AB} on coalescence time of two immiscible droplets is shown in Fig. 5c. The results demonstrated that the coalescence time decreased with the increase of θ_{AB}, which means that coalescence of two immiscible drop happened more quickly when the equilibrium structure of Janus emulsion tends to be 'complete engulfing'. This may be due to the increase of interfacial driving force with the increase of θ_{AB}.
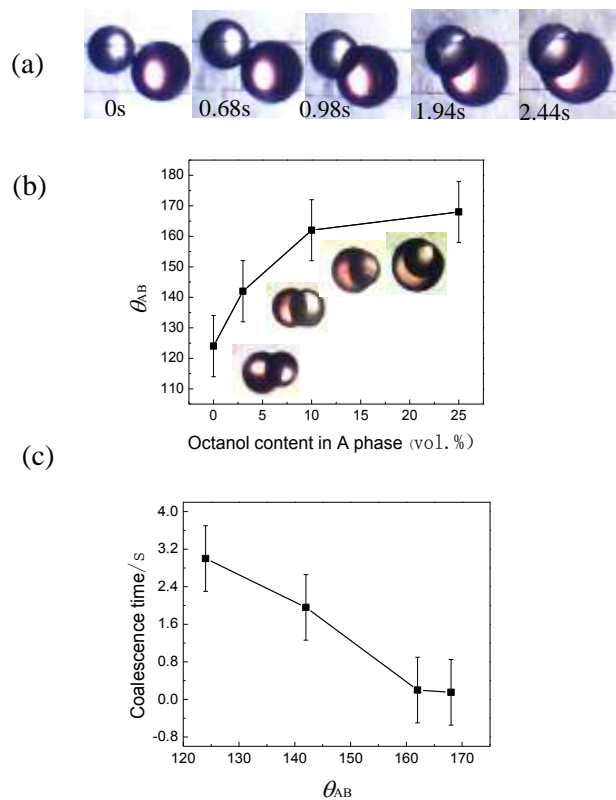
Figure 5. (a) Typical dynamic process of coalescence with different time after the contact of two immiscible droplet. The equilibrium contact angle θ_{AB} is 142° and coalescence time is 1.94s for this system; (b) the effect of octanol concentration in phase A on equilibrium Janus emulsion structure; (c) the effect of the contact angle on the coalescence time of two immiscible droplets.

Table 3 The interfacial tensions of Janus emulsions with different concentration of octanol in soybean oil.

concentration of octanol in soybean oil/vol.%	0	3	10	25
γ_A/mN m^{-1}	1.67	1.65	1.07	0.64
γ_{AB}/mN m^{-1}	23.17	21.84	13.6	11.08

Then, we fixed soybean oil containing 1.5 wt.% PGPR as phase A and silicone oil containing 0.5 wt.% DC 749 as external phase, and changed phase B as deionized water with different concentration of SDS. When the SDS concentration in phase B increased from 0 to 1.0 wt.%, we found the interfacial tensions γ_{AB} decreased more than γ_B, so the water drop was engulfed more by the soybean oil drop gradually and the contact angle θ_{AB} of Janus emulsion droplet increased, as shown in Fig. 6a. And the coalescence time of two immiscible droplets decreased as shown in Fig. 6b. The results are similar to that of changing octanol concentration in phase A.
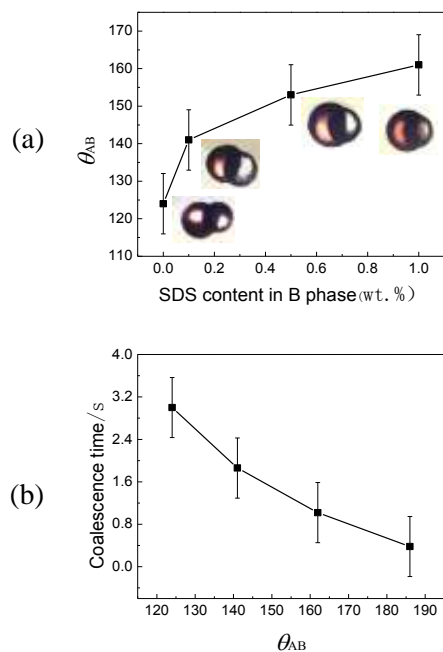
(a)

(b)

Figure 6. (a) The effect of SDS concentration in phase B on Janus emulsion structure; (b) the effect of the contact angle on the coalescence time of two immiscible droplets.

Table 4 The interfacial tensions of Janus emulsions with different concentration of SDS in water.

concentration of SDS in water/wt.%	0	0.1	0.5	1
γ_B/mN m^{-1}	30.36	9.35	7.93	7.35
γ_{AB}/mN m^{-1}	21.82	1.40	1.00	0.94

Finally, we fixed soybean oil containing 1.5 wt.% PGPR as phase A and deionized water containing 0.1 wt.% SDS as phase B, and changing external phase as silicone oil with different concentration of DC 749. When the DC 749 concentration in external phase increased from 1.0 wt.% to 10.0 wt.%, we found the interfacial tensions γ_A and γ_B both decreased with fixed γ_{AB}, so the water drop and the soybean oil drop separated gradually and the contact angle θ_{AB} of Janus emulsion decreased, as shown in Fig. 7a. Furthermore, the coalescence time of two immiscible droplet increased as shown in Fig. 7b. The results demonstrated that two immiscible drop coalescence happened more slowly when the equilibrium structure of Janus emulsion tends to be 'non-engulfing'.
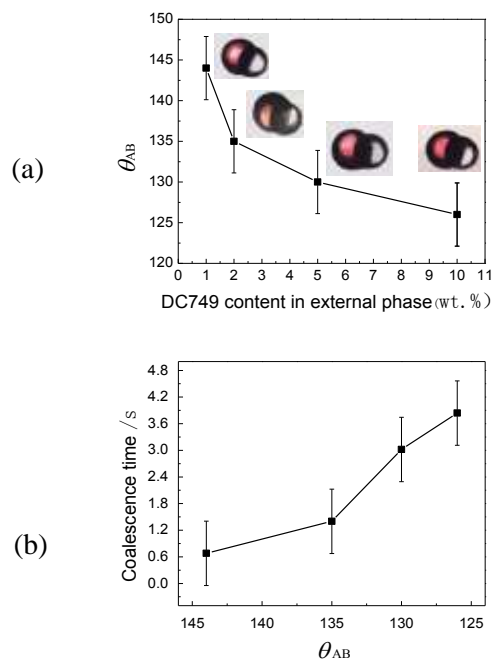
(a)

(b)

Figure 7. (a) The effect of DC 749 concentration in external phase on Janus emulsion structure; (b) the effect of the contact angle on the coalescence time of two immiscible droplets.

Table 5 The interfacial tensions of Janus emulsions with different concentration of DC 749 in silicone oil.

concentration of DC 749 in silicone oil /wt.%	1	2	5	10
γ_A/mN m^{-1}	0.58	0.53	0.36	0.27
γ_B/mN m^{-1}	8.58	8.43	6.88	4.52

From all the above results, by changing the concentration of additive in one phase with the other two phases fixed, we found that the concentration of octanol in soybean oil, SDS in water and DC 749 in silicone oil affected Janus emulsion equilibrium structure and coalescence time, which is very helpful for the controlled preparation of Janus emulsions with different structures. We could control the equilibrium contact angle θ_{AB} in the range of 120°~190° under the experimental conditions, as shown in Fig. 8. Furthermore, we investigated the relationship between thermodynamic equilibrium state of Janus emulsion and coalescence time of two immiscible droplets to form a Janus emulsion of equilibrium, as shown in Fig. 9. We firstly found that the coalescence process of two immiscible droplets would be quicker when the equilibrium structure of Janus emulsion tends to be 'complete engulfing'. The results will be helpful for preparing Janus emulsions with controlled structures by coalescing two immiscible drops in microfluidic device.
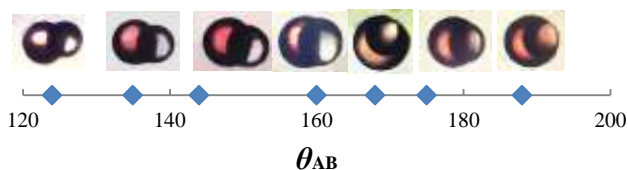
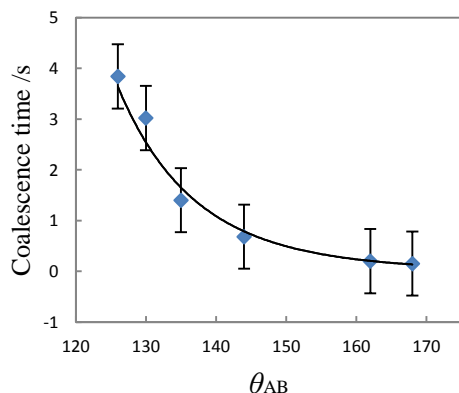Figure 8. The equilibrium structures of different Janus emulsions under different experimental conditions

Figure 9. The relationship between contact angle of Janus emulsion and coalescence time

Conclusions

In this paper, we developed a simple microfluidic device to prepare Janus emulsion by controlled coalescing of two immiscible drops. And we could easily control the number of two immiscible drops and size of them in Janus emulsion by changing the three phase flow rates. Then we changed the experimental systems and systematically investigated the influences of interfacial tensions on the coalescing dynamics and thermodynamic equilibrium structures. We found the concentration of n-octanol in soybean oil, SDS in water and DC 749 in silicone oil affected the coalescence time and equilibrium structure of Janus emulsion. We could control the equilibrium contact angle θ_{AB} in the range of 120°~190° under the experimental conditions. Finally, we firstly found that the coalescence process of two immiscible droplets would be quicker when the equilibrium structure of Janus emulsion tends to be 'complete engulfing'. The results will be helpful for preparing Janus emulsions with controlled structures by coalescing two immiscible droplets in microfluidic device.

Acknowledgements

Notes and references

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