CO₂-Switchable Microemulsion Based on a Pseudogemini Surfactant

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1. CO₂-Responsive Microemulsion.

Just as shown in Scheme S1, a typical experiment used 15 mL of microemulsion placed in a test three flask with a magnetic stirring and a condenser. First of all, dry CO_2 was bubbled through the solution at a rate of 20 mL·min⁻¹ for 30 min at 25 ± 0.1 °C, and then the sample was sealed and standing. Then, dry N₂ was bubbled through the solution at a rate of 20 mL·min⁻¹ for 3 h at 50 ± 0.1 °C, and then the sample was sealed and standing. Under the aforementioned condition, the loss of the volatile species (n-heptane was thought as the volatile specie in our work) could be remarkably minimized.



Scheme S1. Experimental setup of CO₂-switchable microemulsion.

2. The Role of TMPDA in CO₂-switchable Microemulsion

The similar microemulsion without TMPDA could also be CO_2 -switchable? we have prepared a microemulsion that composed with SDS (15%), n-hexane (20%), n-butanol (15%) and water (50%). At 25°C, CO_2 was bubbled into the microemulsion and the flow rate is control in $0.2L \cdot min^{-1}$. At the same time, the experimental phenomena should be record.



Figure S1. The effect of CO₂ on microemulsion without TMPDA

From Figure S1, the microemulsion without TMPDA has no obvious change with CO₂ bubbling after 30 min, that means the microemulsion without TMPDA has no CO₂-switchable performance. Accordingly, The TMPDA molecules plays an important role in CO₂-switchable microemulsion system. In essence, the CO₂-switchable of microemulsion was caused by tertiary amine and surfactant self-assembly in microemulsion system with CO₂ and N₂ bubbling and the TMPDA is indispensable. Monomeric counterparts SDS and TMPDA cannot achieve the CO₂/N₂ "switch" process of microemulsions. Only SDS / TMPDA co-exist with Pseudogemini Surfactant can achieve the microemulsion switching process.

3. Effects of TMPDA and n-butanol on n-hexane/water interfacial tension

The interfacial tension between n-hexane and surfactant aqueous was determined by spinning drop technology on XZD-SP spinning drop interfacial tensiometer (Beijing Ha Ke Test Instrument Factory). The water phase was injected into the quartz tube firstly, and then the oil phase was put

into the middle of the tube by micro-injector. Finally, the tube was enveloped with a plastic cover and put into the apparatus following by rotating with the velocity of 4000 rpm in all cases. All the measurements were carried out at 25.0 ± 0.1 °C.

As we all know, Formation of microemulsion requires ultralow oil-water interfacial tension. SDS can effectively reduce the interfacial tension between oil and water, but cannot make it to ultralow state¹. How does the TMPDA and n-butanol affect the interfacial tension of oil and water?

Table S1. The interfacial tension between different water phase and oil phase

Water phase	Oil phase	Interfacial
water plase	On phase	tension/mN·m ⁻¹
H ₂ O	n-hexane	46.82
0.5526g TMPDA+10g H ₂ O	n-hexane	25.51
0.5526g TMPDA+10g H ₂ O	4g n-hexane+3g n-butanol	3.48

As shown in Table S1, the interfacial tension of water and n-hexane was 46.82 $\text{mN}\cdot\text{m}^{-1}$, However, the addition of TMPDA makes the interfacial tension drop to 25.51 $\text{mN}\cdot\text{m}^{-1}$, The interfacial tension can be further reduced to 3.48 $\text{mN}\cdot\text{m}^{-1}$, when n-butanol was introduced. The result in table S2 shows that TMPDA and n-butanol play a vital role in the formation of microemulsion.

The composition of the aqueous and oil phase are listed in Table S2, and the interfacial tension of water phase and oil phase in entry A, B, C, D, E and F were obtained as shown in Figure S2.

Table S2. The different composition of the oil and the water phase

Entry	Water phase	Oil phase		
		n-hexane(g)	n-butanol(g)	TMPDA(g)
А	4.8948gSDS+20gH ₂ O	8	0	0
В		8	2	0.3684
С		8	4	0.7368
D		8	6	1.1052
Е		8	8	1.4736



Figure S2. The interfacial tension of the oil phase and the aqueous phase

corresponding to the table S2

With the increase of the TMPDA and n-butanol, the interfacial tension of water and n-hexane has a significantly reduced. Under the condition of low n-butanol and TMPDA concentration, the interfacial tension of oil and water changes slowly with time. Oil and water interfacial tension decreased very rapidly, in the high co-surfactant concentration, and the interfacial tension to ultralow value.

4. Effect of n-Butanol on Micellar Formation

When the carbon dioxide was introduced into the microemulsion, the microemulsion undergoes phase separation. The lower phase surfactant aqueous solution(SDS-TMPDA-SDS) did not form a worm-like micelle with a larger viscosity.

The SDS and TMPDA were dissolved in deionized water at room temperature, the molar ratio of SDS to TMPDA was 2:1, and then, n-butanol at a mass concentration of 15% was added to this aqueous solution. Carbon dioxide was introduced into the solution, and the viscosity change of the solution was observed.



Figure S3. Surfactant and n-butanol aqueous solution with and without CO_2 (a)

SDS+TMPDA+n-butanol+H₂O,(b) SDS+TMPDA+n-butanol+H₂O+CO₂

As the Figure S3 shows, The viscosity of SDS,TMPDA and n-butanol aqueous solution did not changed significantly before (Figure S3 (a)) and after (Figure S3 (b)) CO_2 introduced. SDS and TMPDA aqueous solution can form worm-like micelles at molar ratio of 2:1 after the introduction of CO_2^2 . But in our work, the worm-like micelles did not form.



Figure S4. The effect of n-butanol on the behavior of SDS and TMPDA aqueous solution

The alcohols are believed to be solubilized in the interfacial region of the micelles, so that their polar functional groups (OH for example) can retain their contact with water³. The reason for the failure of worm-like micelles formation may be due to the solubilization of n-butanol in the surfactant molecule. As the figure S4 shows, The n-butanol molecules could solubilize in the SDS-TMPDA-SDS molecules, and the effective head group area of surfactant was larger than no n-butanol solution, it showing a conical shape, which is more favorable for the formation of spherical micelles than worm-like micelles⁴.



Figure S5. The mechanism of CO₂-switchable microemulsion

References

- 1. Y. Zhang, Y. Zhang, C. Wang, X. Liu, Y. Fang and Y. Feng, *Green Chem.*, 2016, **18**, 392-396.
- 2. Y. Zhang, Y. Feng, Y. Wang and X. Li, *Langmuir*, 2013, 29, 4187-4192.
- 3. Q. Shen, G. Z. Li, C. S. Ma, S. X. Hao, X. L. Wei and Y. Z. Huang, *Chinese Journal* of *Chemistry*, 1997, **15**, 405-409.
- 4. J. Israelachvili, S. Marčelja and R. G. Horn, *Quarterly reviews of biophysics*, 1980, **13**, 121-200.