

# Study on the Influence of Hydrophilic Nano-SiO<sub>2</sub> on the Properties of Water-in-Oil Emulsions with Different Co-Emulsifiers

DongPing Yuan<sup>1\*)</sup>, ShaSha Xu<sup>1)</sup>

College of Petroleum Engineering, Yangtze University, Wuhan, China

**ABSTRACT:** Water-in-oil (W/O) emulsions tend to suffer from interfacial film rupture, droplet coalescence, and stability degradation in deep-well high-temperature drilling operations above 120°C, which severely compromises drilling fluid performance. To improve the stability of W/O emulsions, this study used Span80 as the primary emulsifier, compounded with four co-emulsifiers—OP-4, CTAB, SDBS, and EAB40—to investigate the changes in emulsion properties before and after adding 0.25% hydrophilic nano-silica (SiO<sub>2</sub>). The regulation mechanism of hydrophilic nano-SiO<sub>2</sub> on the emulsion system was systematically analyzed by testing demulsification voltage, rheological properties, centrifugal stability, and contact angle of samples under two conditions: stirring for 4 h and aging at 120°C for 4 h. After particle addition, the demulsification voltage of each system increased to varying degrees; the OP-4 system reached as high as 630 V, and the oil–water interface remained the most stable during centrifugation. The results show that hydrophilic nano-SiO<sub>2</sub> significantly enhances the interfacial strength and high-temperature stability of emulsions, effectively inhibiting droplet coalescence and phase separation at high temperatures. The synergistic effect between different types of co-emulsifiers and nanoparticles differs significantly, and the OP-4 composite system exhibits the best overall stabilization effect. After high-temperature aging, the samples with nano-SiO<sub>2</sub> have higher demulsification voltage, more stable rheological parameters, lower centrifugal liquid separation rate, and smaller contact angle. The findings provide an experimental basis for formula optimization and engineering applications of stable W/O emulsions for high-temperature drilling.

**KEYWORDS:** oil-based drilling fluid; water-in-oil emulsion; hydrophilic nano-SiO<sub>2</sub>; high temperature; stability

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## I. Introduction

Oil-based drilling fluids are widely used in deep, ultra-deep, and high-temperature oil–gas drilling. However, in downhole environments above 120°C, the emulsions constituting drilling fluids are prone to interfacial film damage, droplet coalescence, and phase separation, leading to drilling fluid performance failure and engineering accidents such as increased fluid loss, wellbore instability, and pipe sticking, which seriously threaten drilling safety [1–3]. The high-temperature stability of W/O emulsions is mainly determined by the strength of the oil–water interfacial film. High temperature reduces the adsorption capacity of emulsifiers at the interface, loosens and weakens the interfacial film, and makes emulsions more susceptible to demulsification under shearing in drilling fluids [3–6]. Currently, conventional emulsifier systems lack sufficient stability at high temperatures, and research on the synergistic enhancement of high-temperature emulsion stability by nanomaterials and compound emulsifiers is insufficient to meet the requirements of high-temperature drilling engineering [4][7]. Therefore, this study uses Span80 as the primary emulsifier compounded with OP-4, CTAB, SDBS, and EAB40, and investigates the changes in demulsification voltage, rheology, centrifugation, and contact angle of emulsions at 20 °C and after aging at 120°C before and after adding 0.25% hydrophilic nano-SiO<sub>2</sub>. The influence law of 0.25% hydrophilic nano-SiO<sub>2</sub> on different emulsifier systems is analyzed, and formulations with better high-temperature stability are optimized to provide technical support for field applications of high-temperature drilling fluid systems.

## 1 Experimental Part

### 1.1 Materials

The base oil for preparing W/O emulsions was 5# white oil, purchased from Pengrunxing Lubricating Oil Co., Ltd., Dongguan City, Guangdong Province; deionized water was supplied by a laboratory ultrapure water system for sample dilution and solution preparation. Anhydrous CaCl<sub>2</sub> was purchased from Xilong Scientific—Guangdong Fine Chemicals Engineering Research and Development Center; Span80 was purchased from Xilong Scientific—Guangdong Fine Chemicals Engineering Research and Development Center; OP-4, a nonionic emulsifier, was purchased from Shandong Yousuo Chemical Technology Co., Ltd.; EAB40, an amphoteric emulsifier, was purchased from Shanghai Yincong New Material Technology Co., Ltd.; SDBS, an anionic emulsifier (chemically pure), was purchased from Xilong Scientific; CTAB, a cationic emulsifier, was purchased from Shanghai Macklin Biochemical Co., Ltd. The active ingredient used was 0.25 wt% nano-SiO<sub>2</sub> hydrophilic grade (TSP-H10, 99.0%), with a specific surface area of 180 m<sup>2</sup>/g and particle size of 20 nm, purchased from Shanghai Macklin Biochemical Co., Ltd. In this experiment, Span80 was fixed as the primary emulsifier and mixed with different co-emulsifiers to prepare emulsions. The compounding of primary and co-emulsifiers adjusted the HLB value of the emulsifier mixture to 5.2–5.4 for satisfactory emulsification. The formulations of each group are shown in Table 1.

Table 1 Emulsifier formulations and their HLB values

Primary–co-emulsifier composite system	Weighted HLB value
4.5wt%Span80+1.5wt%OP-4	5.30
5.5wt%Span80+0.5wt%CTAB	5.26
5.0wt%Span80+1.0wt%SDBS	5.35
4.5wt%Span80+1.5wt%EAB40	5.30

### 1.2 Instruments

ZNN-D6 six-speed rotational viscometer, purchased from Qingdao Chuangmeng Instrument Co., Ltd.; Fann-23E electrical stability tester, purchased from Fann Instrument Company (Houston, Texas, USA); BM2000 biological microscope, purchased from Jiangnan Yongxin Optical Co., Ltd.; LC-05A medical centrifuge, purchased from Jiangsu Zhengji Instrument Co., Ltd.; XGRL-4A high-temperature roller heating furnace, purchased from Qingdao Chuangmeng Instrument Co., Ltd.; JPS-20B ultrasonic disperser, purchased from Ningbo Xinzhi Biotechnology Co., Ltd.; GJS-B12K variable-speed high-frequency mixer, purchased from Qingdao Haitongda Special Instrument Co., Ltd.

### 1.3 Preparation of White Oil Emulsions

Emulsions were prepared at an oil–water volume ratio of 7:3 (224 mL oil phase, 96 mL water phase). The primary emulsifier Span80 and co-emulsifiers (CTAB, OP-4, SDBS, EAB40) were mixed in the oil phase at specified ratios. A certain amount of CaCl<sub>2</sub> was added to the water phase to form a 20 wt% CaCl<sub>2</sub> solution. The water-phase system was mixed in a high-speed mixer at 10,000 rpm for 30 min for preliminary homogenization. A certain volume of liquid was taken from the stirred water phase, mixed with 0.25 wt% hydrophilic nano-SiO<sub>2</sub> to prepare a CaCl<sub>2</sub> aqueous solution containing particles, and dispersed under ultrasonication for 30 min with continuous stirring to ensure uniform dispersion of nano-SiO<sub>2</sub> and avoid agglomeration. The particle-containing CaCl<sub>2</sub> aqueous solution was then slowly added dropwise to the oil phase under stirring at 4,000 rpm. After complete addition, the mixture was stirred at 10,000 rpm for 2 h to obtain stable nanoemulsions. For the control W/O emulsions, the 20 wt% CaCl<sub>2</sub> aqueous solution stirred for 30 min was directly added dropwise to the oil phase, followed by stirring at 10,000 rpm for 2 h; other conditions were consistent with the experimental group.

### 1.4 Test Methods for Emulsion Properties

Rheological properties were measured using a ZNN-D6 six-speed rotational viscometer (Qingdao Chuangmeng Instrument Co., Ltd.). Electrical stability was tested with a Fann-23E electrical stability tester: a voltage was applied to the emulsion via electrodes until the sample demulsified and became conductive, and the peak voltage recorded automatically was defined as the demulsification voltage. A higher value indicates stronger

interfacial film strength and better stability of emulsion droplets. Centrifugal stability was measured using an LC-05A medical centrifuge: 14 mL of emulsion was added to a centrifuge tube, and the initial volume was recorded. Centrifugation was performed at 20 °C and 10,000 rpm; the volume of separated free liquid was read at intervals, and the oil separation rate was calculated as follows:

$$R_{oil} = \frac{V_{oil}}{V_{em}} \times 100\% = \frac{h_{oil}}{h_{em}} \times 100\%$$

where  $R_{oil}$  = oil separation rate (%),  $V_{oil}$  = volume of separated oil (mL),  $V_{em}$  = initial emulsion volume (mL),  $h_{oil}$  = height of separated oil (cm),  $h_{em}$  = total emulsion height (cm).

A lower oil separation rate indicates stronger resistance to phase separation. Contact angle was measured using an OCA25 optical contact angle meter (DataPhysics Instruments GmbH, Filderstadt, Germany): a micro-sampler was used to deposit emulsion droplets on a glass slide, and the contact angle of droplets on the solid surface was measured. The contact angle reflects the wettability of the emulsion to solids. Aging tests were conducted in an XGRL-4A high-temperature roller heating furnace: emulsions were loaded into aging cans and rolled at 120°C for 4 h, then cooled naturally to room temperature for subsequent performance evaluation.

## II. Results and Discussion

### 2.1 Effect of Hydrophilic Nano-SiO<sub>2</sub> on Emulsion Rheology

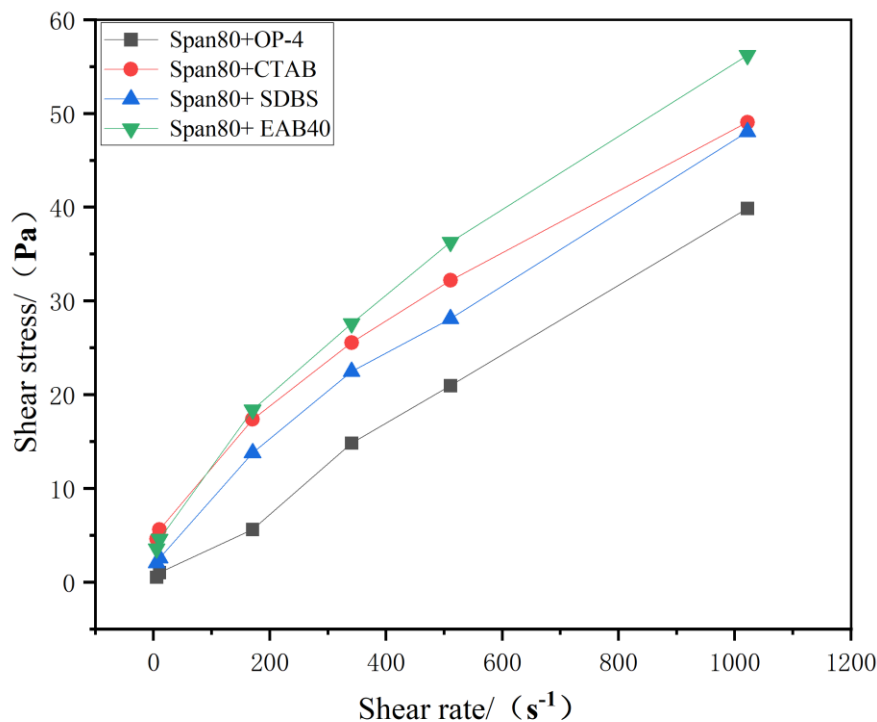


Figure 1 Rheological curves of different emulsion formulations after stirring for 4 h

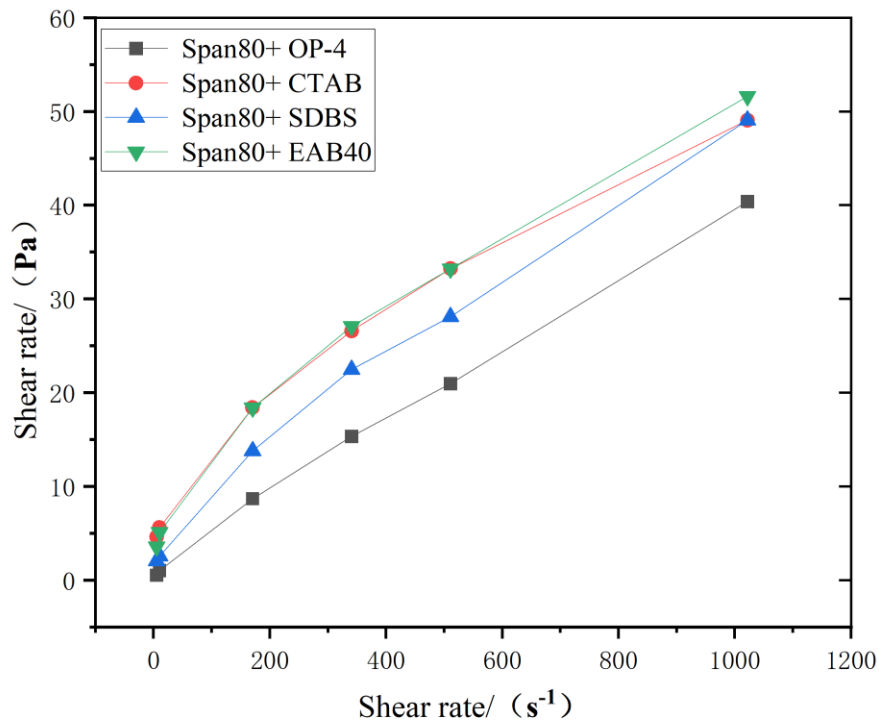


Figure 2 Rheological curves of different emulsion formulations with hydrophilic nano-SiO<sub>2</sub> after stirring for 4 h

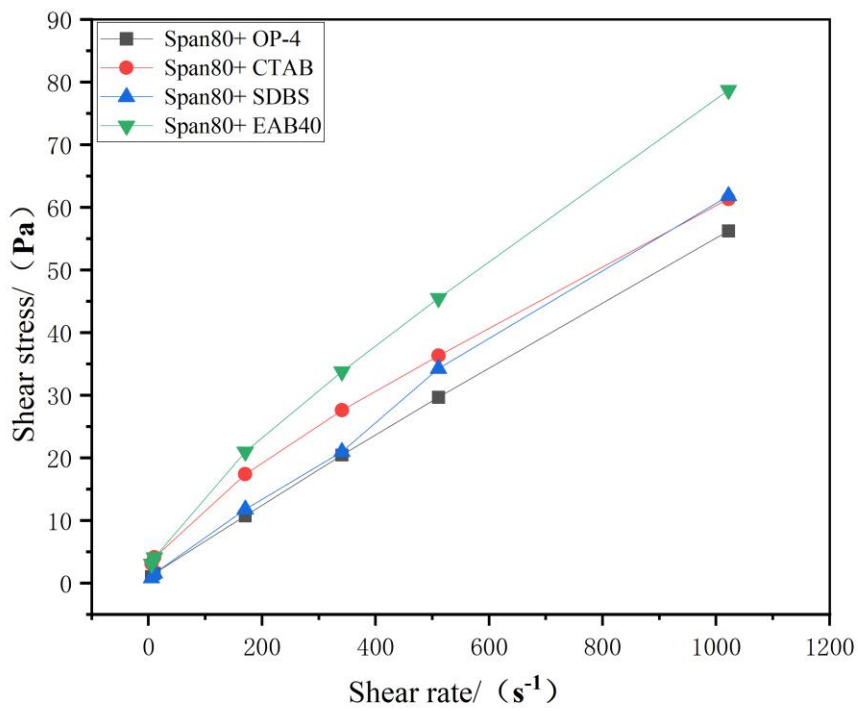


Figure 3 Rheological curves of different emulsion formulations after stirring for 4 h and aging

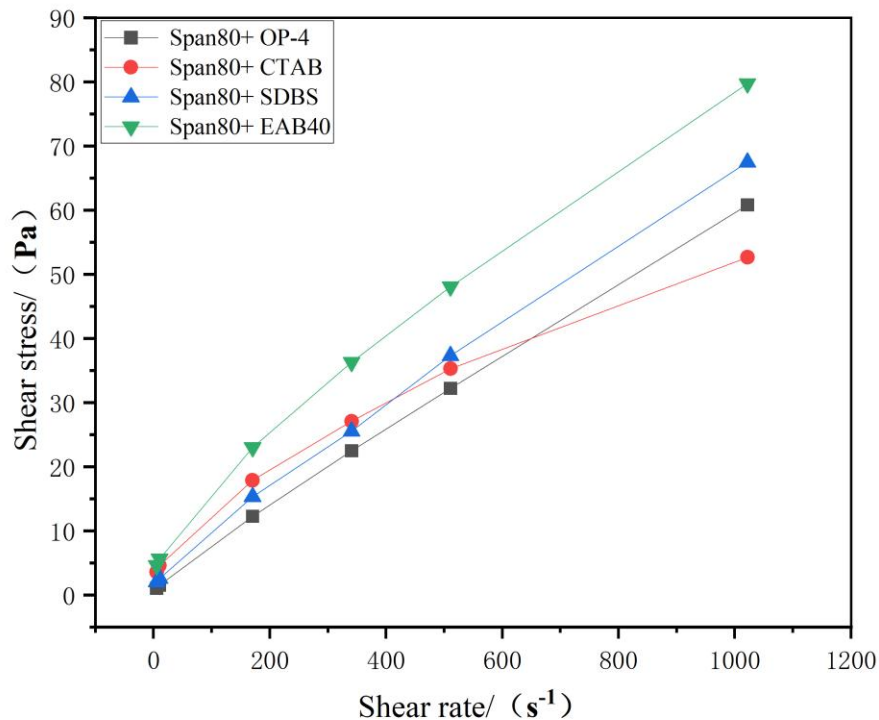


Figure 4 Rheological curves of different emulsion formulations with hydrophilic nano-SiO<sub>2</sub> after stirring for 4 h and aging

Rheological test results show that hydrophilic nano-SiO<sub>2</sub> significantly enhances the structural strength and rheological stability of W/O emulsions. In emulsions stirred for 4 h without SiO<sub>2</sub> the shear stresses of OP-4, CTAB, SDBS, and EAB40 systems at 1000 s<sup>-1</sup> were 39 Pa, 49 Pa, 48 Pa, and 56 Pa, respectively. After introducing 0.25% hydrophilic nano-SiO<sub>2</sub>, the shear stress of each system increased synchronously, attributed to the adsorption of nanoparticles at the oil–water interface, which strengthened the compactness of the interfacial film and thereby improved emulsion rheology [8].

After high-temperature aging, the shear stress of systems without SiO<sub>2</sub> increased significantly due to droplet coalescence and increased system viscosity. Systems with SiO<sub>2</sub> showed differences: the OP-4 system formed a strongly synergistic composite interface with SiO<sub>2</sub> and emulsifiers, effectively inhibiting droplet coalescence and achieving optimal structural stability, while CTAB, SDBS, and EAB40 systems had much weaker stabilization effects due to poor interfacial interactions.

2.2 Effect of Hydrophilic Nano-SiO<sub>2</sub> on Emulsion Demulsification Voltage

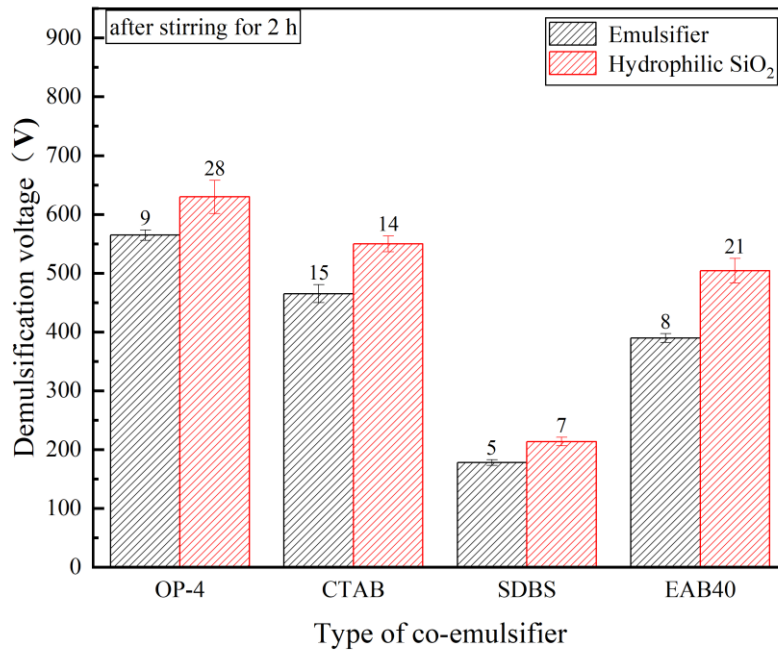


Figure 5 Demulsification voltage images of different emulsion formulations

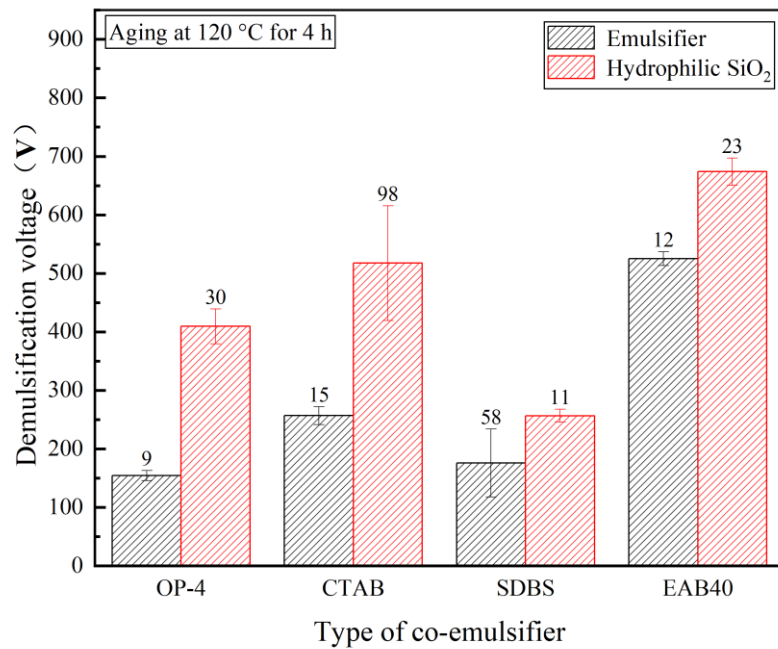


Figure 6 Demulsification voltage images of different emulsion formulations after aging at 120°C for 4 h

Demulsification voltage is a core indicator for evaluating the electrical stability of emulsions; a higher value represents stronger resistance to interfacial film rupture and better electrical stability [9]. Experimental results show that after introducing 0.25% hydrophilic nano-SiO<sub>2</sub> into W/O emulsions formulated with OP-4, CTAB, SDBS, and EAB40, the demulsification voltage of each system increased significantly from 560 V, 480 V, 180 V, and 390 V to 630 V, 550 V, 210 V, and 500 V, respectively, confirming that nano-SiO<sub>2</sub> enhances emulsion electrical stability by strengthening the interfacial film structure [10].

High-temperature aging causes desorption and cracking of emulsifiers, damaging interfacial integrity and reducing the demulsification voltage of all systems to varying degrees. However, aged systems with SiO<sub>2</sub> still maintained a significant voltage advantage over corresponding systems without particles, proving that the composite interfacial film constructed by nano-SiO<sub>2</sub> and emulsifiers effectively resists high-temperature damage and significantly improves the anti-aging performance and long-term stability of emulsions.

### 2.3 Particle Size Distribution of Emulsions with Nano-SiO<sub>2</sub>

Combined with particle size test results, the introduction of hydrophilic nano-SiO<sub>2</sub> led to significant differences in emulsion stability among different co-emulsifier systems. Before aging, the particle size order was SDBS > CTAB > EAB40 > OP-4, indicating that nonionic OP-4 and EAB40 had significant synergistic effects with SiO<sub>2</sub>. Particles and emulsifiers co-accumulated at the oil-water interface to form a dense, high-strength composite interfacial film, effectively inhibiting droplet coalescence [6]. After aging, the average particle size of all systems increased. The OP-4 system maintained the smallest average particle size ( $1.86 \pm 0.61 \mu\text{m}$ ) with optimal stability. Hydrophilic nano-SiO<sub>2</sub> showed poor interfacial adsorption in the SDBS system, resulting in the largest particle size ( $2.16 \pm 0.98 \mu\text{m}$ ), poor dispersion, and easy aggregation, making this system the least stable.

Table 2 Changes in average particle size of emulsions prepared with different co-emulsifiers before and after aging

Emulsion	Average particle size before aging D (um)	Average particle size after aging D (um)
Span80+OP-4	$1.09 \pm 0.32$	$1.86 \pm 0.61$
Span80+CTAB	$1.12 \pm 0.38$	$2.55 \pm 0.84$
Span80+EAB40	$1.38 \pm 0.36$	$2.12 \pm 0.63$
Span80+SDBS	$1.61 \pm 0.61$	$2.09 \pm 1.08$

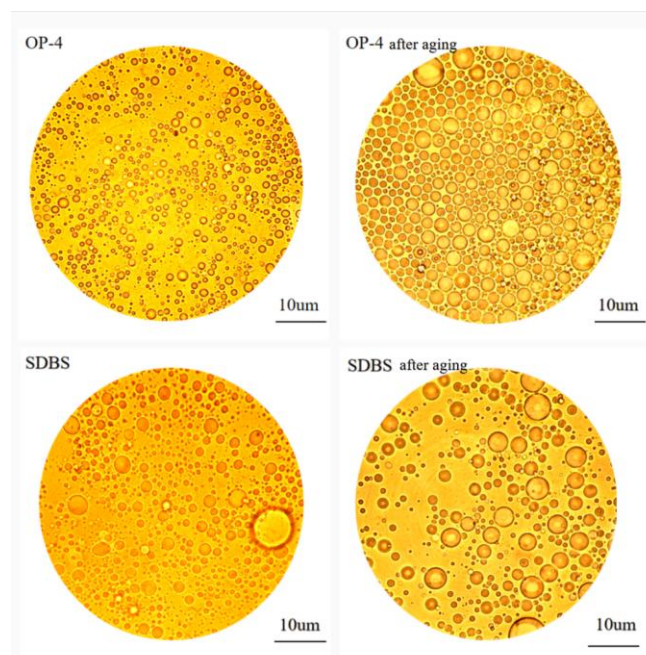


Figure 7 Particle size images of OP-4 and SDBS systems before and after aging

## 2.4 Effect of Hydrophilic Nano-SiO<sub>2</sub> on Contact Angle

Table 3 Effects of hydrophilic nano-SiO<sub>2</sub> and aging conditions on contact angles of different emulsifier systems

Condition	OP-4/(°)	CTAB/(°)	SDBS/(°)	EAB40/(°)
Without SiO <sub>2</sub> – stirred for 2 h	12.5	15.7	29.1	13.7
Without SiO <sub>2</sub> – aged for 4 h	23.7	21.6	30.7	14.8
With SiO <sub>2</sub> – stirred for 2 h	10.8	15.6	28.9	13.6
With SiO <sub>2</sub> – aged for 4 h	22.5	21.5	30.2	14.1

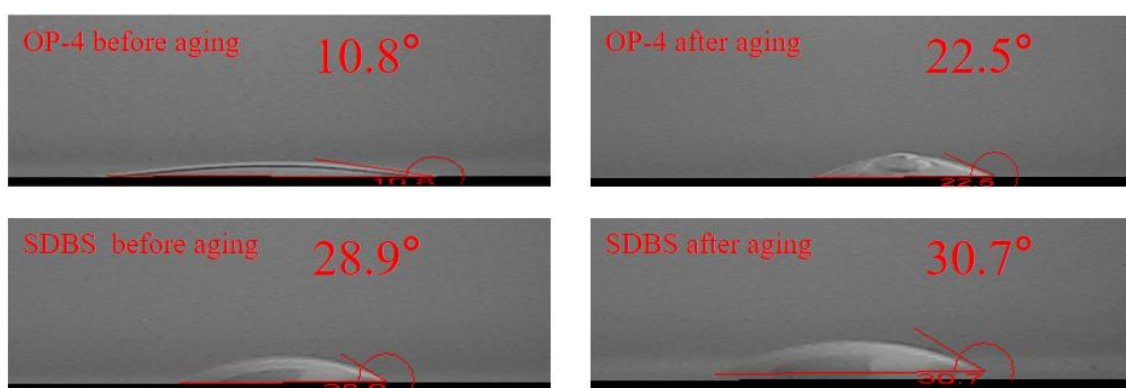


Figure 8 Contact angle images of OP-4 and SDBS systems before and after aging

Contact angle is a core indicator characterizing particle interfacial wettability and adsorption behavior; its change directly reflects the arrangement of particles at the oil–water interface and thus determines emulsion stability. Data show that after introducing hydrophilic nano-SiO<sub>2</sub>, the contact angle of each system decreased, with the OP-4 system decreasing by 1.7° (the largest drop, ~13.6%), indicating that nanoparticles synergize with emulsifiers to promote denser and more ordered interfacial molecular arrangement, significantly improving interfacial stability.

After high-temperature aging, the contact angle of all systems increased, but systems with SiO<sub>2</sub> remained significantly lower than corresponding systems without particles. This confirms that the synergistic effect of nanoparticles and emulsifiers effectively alleviates emulsifier desorption and cracking caused by high temperature, thereby significantly improving the interfacial hydrophobicity and long-term thermal stability of the system.

2.5 Effect of Nano-SiO<sub>2</sub> Wettability on Emulsion Dynamic Stability

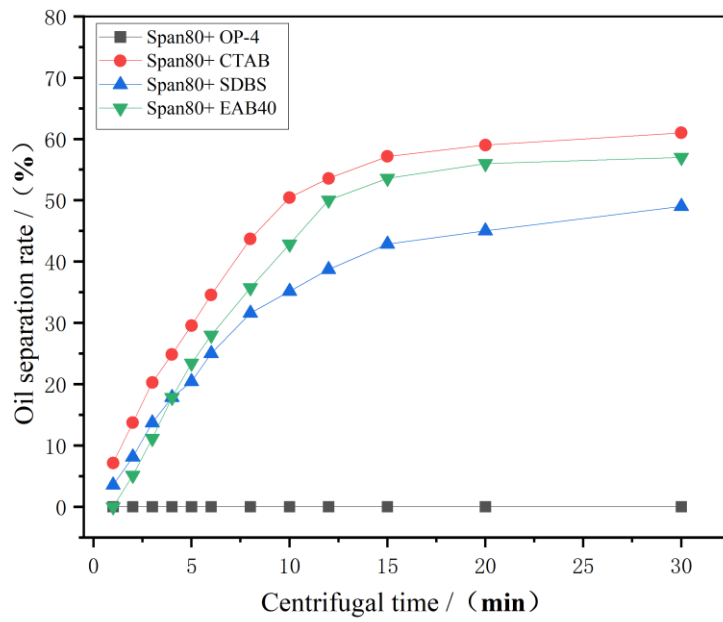


Figure 9 Centrifugal curves of different emulsion formulations after stirring for 4 h

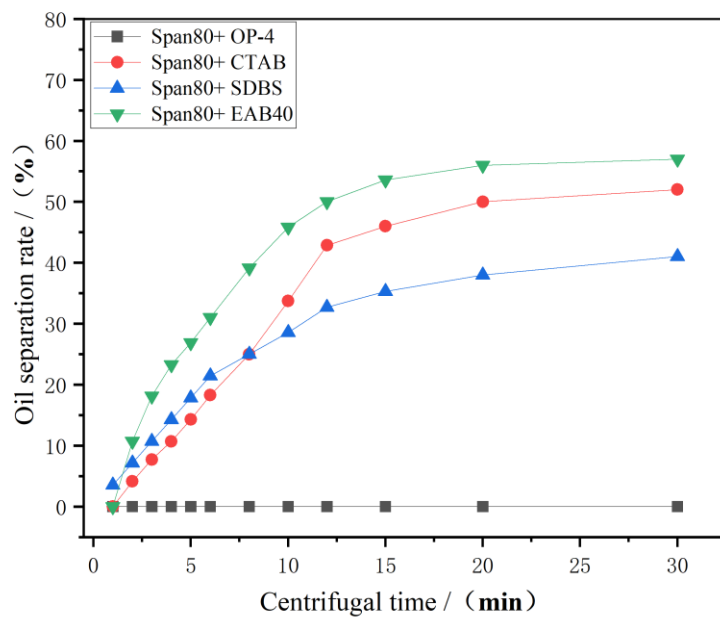


Figure 10 Centrifugal curves of hydrophilic nano-SiO<sub>2</sub> groups after stirring for 4 h

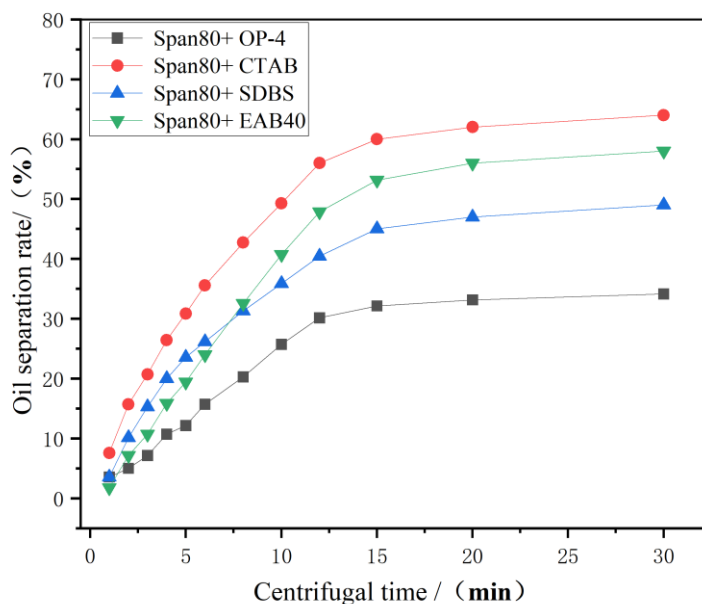


Figure 11 Centrifugal curves of different emulsion formulations after aging at 120°C

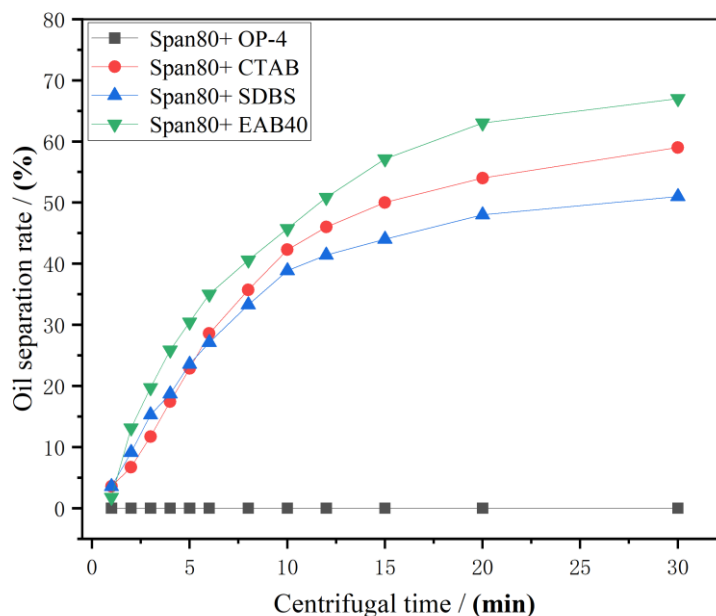


Figure 12 Centrifugal curves of hydrophilic nano-SiO<sub>2</sub> groups after aging at 120°C

Centrifugal stability tests show that the Span80–OP-4 composite system exhibits the best dynamic stability: the oil separation rate was always the lowest in the unaged stage, significantly better than CTAB, SDBS, and EAB40 systems. After thermal aging at 120°C, the oil separation rate of all systems without hydrophilic SiO<sub>2</sub> increased significantly; at 30 min centrifugation, the oil separation rate of the OP-4 system rose to 38%, and other systems exceeded 50%, confirming that high temperature significantly reduces droplet interfacial film strength and degrades dynamic stability [11].

After adding hydrophilic SiO<sub>2</sub>, the aged Span80–OP-4 system maintained 0% oil separation rate, and the oil separation rates of CTAB, SDBS, and EAB40 systems were also significantly lower than those of the control group without particles. This is attributed to the synergistic effect between hydrophilic SiO<sub>2</sub> and emulsifiers, which forms a high-strength composite interfacial film and improves the thermal aging resistance of emulsions. The weaker interfacial adsorption between SiO<sub>2</sub> and ionic (CTAB, SDBS) and amphoteric EAB40 emulsifiers fails to form a stable structure, resulting in poorer stability than the OP-4 composite system.

### Conclusions

- 1) Different co-emulsifier systems compounded with Span80 are prone to emulsifier desorption and even cracking from the oil–water interface under 120°C high-temperature aging, leading to significant degradation of key properties such as dynamic stability, electrical stability, and wettability of emulsions.
- 2) In oil-based drilling fluid systems, hydrophilic nano-SiO<sub>2</sub> not only significantly enhances the high-temperature anti-aging performance, dynamic stability, and electrical stability of emulsions by strengthening the oil–water composite interfacial film structure, but also effectively improves the lubricating performance of drilling fluids.
- 3) The strengthening effect of nanoparticles on different co-emulsifier systems differs significantly. The Span80–OP-4 composite system shows the optimal synergistic effect, with a centrifugal oil separation rate below 40% and a demulsification voltage of 630 V. This is attributed to the formation of a structurally stable composite interface in this system, which most significantly improves the overall stability of the emulsion.

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