

개질된 나노 실리카의 오일 분산체 제조와 O/W 에멀전 안정성

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Preparation of Modified Nano-SiO₂ Oil Dispersion System and the Stability of Its O/W Emulsion

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Abstract: Nano-SiO₂ was organically modified with silane coupling agent-KH570 to prepare the modified Nano-SiO₂ oil dispersion system. By increasing the dosage of KH570, the ζ -potential (absolute value) and the char yield values decreased gradually. When KH570 was 5%, the maximum contact angle with water reached 79.8°. Then, the modified Nano-SiO₂ was composed with petroleum sulfonate (PS) and its ability of reducing the O/W interfacial tension was measured. The results showed that, O/W interfacial tension reduced to about 5.86×10^{-3} mN/m when the Nano-SiO₂ and petroleum sulfonate composite was mixed with the mass fraction of 0.2:0.3%. The emulsion stability coefficient was 2.15 after 120 min which was the minimum. It indicated that this compounded system had the best emulsifying ability because Nano-SiO₂ particles were dragged onto the O/W interface by the PS molecules to improve the intensity of O/W interface.

Keywords: Nano-SiO₂, hydrophobic modification, ζ -potential, composite oil dispersion system, enhanced oil recovery.

Introduction

Nano-SiO₂ is a kind of amorphous white powder, which has become one of the highest yield in the world. Because of its unique optical, catalytic and rheological properties, it has been widely studied and applied as a functional inorganic carrier.¹⁻⁴ The traits of nanoparticles are hardly embodied in usage because they are usually dispersed in medium of micro-size aggregation.⁵⁻⁷ The study of improving dispersivity of Nano-SiO₂ in organic solvents has become very popular recently. Because Nano-SiO₂ can't be sufficiently dispersed on the O/W interface, its surfaces need to be organically modified. Then it can be adsorbed on a stable O/W interface, reduce the interfacial tension and enhance the stability of O/W emulsion, so as to achieve the goal of improving oil recovery.

Currently, Nano-SiO₂ surface was modified by using silane coupling agent^{8,9} and coupling agent of organic titanate.¹⁰ D.C. Su used silane coupling agent to modify Nano-SiO₂ surface

and studied the dispersion stability of modified powder in ethanol (organic solvents). The results showed that after modification treatment, the aggregate block size of powder made by Nano-SiO₂ in an organic solvent was significantly reduced. J. H. Liu^{11,12} and other scholars further studied the varying amount of effects of silane-coupling agent on particle size. When the amount of silane-coupling agent was 5%, the particle size of Nano-SiO₂ in organic solvents decreased to 103 nm. This research provides a guidance for the synthesis of small particle size of Nano-SiO₂.

Above researches proved that Nano-SiO₂ have broad application prospects in enhancing oil recovery. However, the change of surface charge and the mechanism of reducing interfacial tension about the modified Nano-SiO₂ are not systematically studied. In this paper, using a silane coupling agent-KH570, Nano-SiO₂ was organically modified and its ζ -potential was studied. The relationship between zeta potential of modified Nano-SiO₂ and organic modification conditions had been established. Modified Nano-SiO₂ and petroleum sulfonate (PS) were mixed to prepare the nanometer composite system. By studying the changes of ζ -potential on the surface of Nano-SiO₂ and the O/W interfacial tension, the emulsion stability

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mechanism was investigated.

Experimental

Materials. Nano-SiO₂ was obtained from Wacker Chemie AG (Germany, Silane coupling agent-KH570). Ethanol, analytically pure was made by Rui Jinte Chemical Limited Corporation (Tianjin). Crude oil was provided by Shengli Oilfield (Shandong). Petroleum sulfonate (PS) was provided by Shengli Oilfield (Shandong).

Surface Treatments of Nano-SiO₂ Particles. First, 30 g Nano-SiO₂ particles and 500 g ethanol were added to a high-speed dispersion machine filled with zirconium oxide beads and ground for 1~2 h at 4000 rpm. The mixture was filtrated to remove the zirconium oxide beads. Then 4.5 g KH570, which was pre-hydrolysed for 2 h in pH 4.00 ethanol/water (1/9 wt) solution adjusted by acetic acid, was slowly dropped into the solution, and the triethylamine was added until the pH reached 9. After 2 h reaction, the mixture was filtrated to remove the solvent and then it was dried at 120 °C for 4 h to further remove the rudimental solvent. Ground by air current, the Nano-SiO₂ particles treated with KH570 were prepared. The chemical reaction mechanisms of KH570 and Nano-SiO₂ are explained in Figure 1.

Characterization Measurements. The Fourier transform infrared spectroscopy (FTIR) spectra of host polymer and guest polymer were recorded on a Nicolet Nexus 470 spectrometer (on KBr tablets) in the optical range of 400~4000 cm⁻¹ by averaging 32 scans at a resolution of 4 cm⁻¹. The thermogravimetric analysis (TGA) was performed on a Shimadzu TGA-50 instrument at the heating rate of 20 °C/min in air.¹³

Measurement of Water Contact Angle. Using hydraulic machine, the thin slice of Nano-SiO₂ (40 mm in diameter) was prepared. Then, the contract angle with water of these wafers was measured by SL200b (contact angle measurement).¹⁴

Preparation of O/W Crude Oil Emulsion. The O/W crude oil emulsions were prepared by mixing the Shengli crude oil with Shengli simulation formation water containing Nano-SiO₂ systems (1:4 v/v) at 50 °C using a FM-200 homogenizer (Fluko Corp.) at a rotating speed of 3000 rpm for 5 min.

Measurement of O/W Interfacial Tension. The oil/water interfacial tension was measured using the TX-500C dynamic interfacial tension meter at 50±0.1 °C, with a rotating speed of 6000 r/min. The solution was injected into the tube and kept rotating for about 5 min to get pre-equilibrium before injecting 0.5 μL of oil.

Multiple Light Scattering Measurements. 20 mL O/W crude oil emulsions stabilized by Nano-SiO₂ systems were placed into cylindrical glass tubes, and then submitted to a Turbiscan lab expert stability analyzer. The two detectors were used to scan along the height of every O/W crude oil emulsion sealed in tube at 50 °C for 1 h.

Results and Discussion

Spectroscopy and Surface Zeta Potential Analysis. Infrared spectral analysis of Nano-SiO₂ and modified Nano-SiO₂ under different conditions were taken to determine the change of surface molecule structure of Nano-SiO₂. The infrared spectrum was shown in Figure 1.

1110~1000 cm⁻¹ was the stretching vibration absorption peak of Si-O, as well as the characteristic absorption peak of SiO₂. The absorption band at 1730 cm⁻¹ was C=O stretching vibration from KH570. Small absorption peaks at 2930 and 2925 cm⁻¹ were the stretching vibration absorption peak of -CH₂. Before modification, no absorption peaks appeared at 2930 and 2925 cm⁻¹, but the peaks were observed after the modification. And this proved that KH570 had been grafted onto the surface of nanoparticles. The peaks at 2930 and 2925 cm⁻¹ raised along with the amount of silane coupling agent, which indicated that the amount of KH570 was an important factor that affects the surface modification of Nano-SiO₂.

Using Zetasizer 3000 potential meter, the surface ζ-potential of Nano-SiO₂ was measured to study the surface charge properties before and after modification. The results are shown in Table 1. Before modification, the surface ζ-potential of Nano-SiO₂ was -37.6 mV. When modified by KH570, the absolute value of surface ζ-potential decreased with the increase of the dosage of KH570. As shown in Figure 2, there were a large number of hydroxyl groups on the surface of Nano-SiO₂, and they could be ionized in the solution to form negative charges

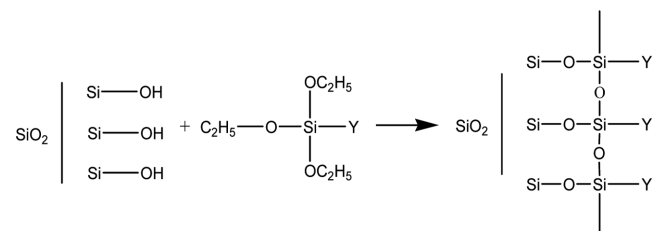
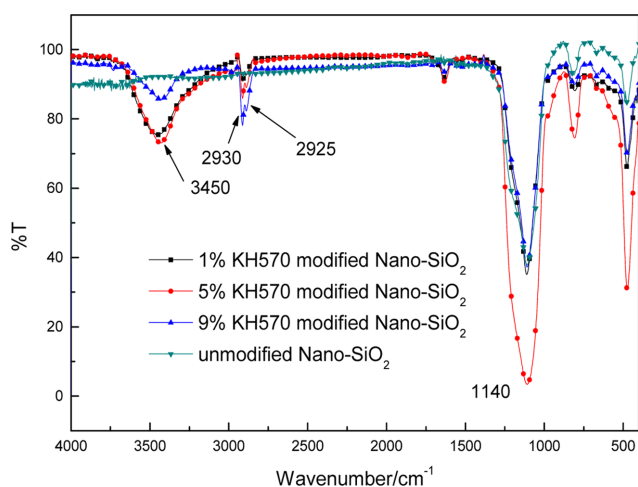


Figure 1. Grafting mechanism of silane on silica particles. Y is the organic functional group.

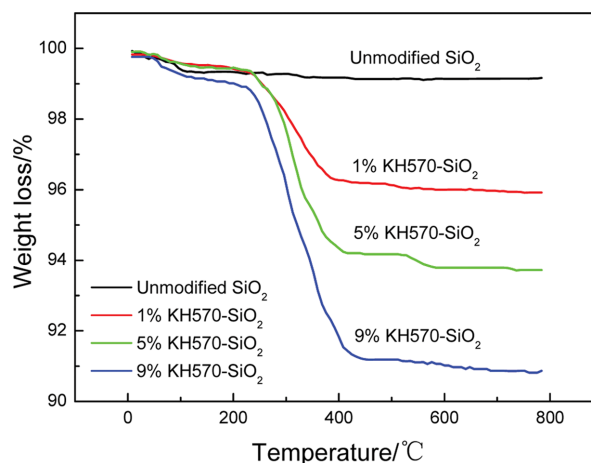
Table 1. ζ -Potential of Nano-SiO₂

KH570 dosage (%)	Nano-SiO ₂ ζ -potential (mV)
0	-37.6
1	-29.5
3	-27.6
5	-23.9
7	-21.8
9	-20.7

**Figure 2.** Infrared spectra of Nano-SiO₂.

on particle surface. When Nano-SiO₂ was organically modified by silane coupling agent-KH570, hydroxyl groups on the surface of Nano-SiO₂ were reacted with KH570. So, the ability of ionization will be reduced and the original electronegativity of the particle surface decreased.

Thermogravimetric Analysis. The thermogravimetric analysis was employed to study the Nano-SiO₂ surface element content changes before and after addition of KH570. Figure 3 illustrates the results of thermogravimetric analysis of Nano-SiO₂ which was modified by KH570. Figure 3 shows that pure Nano-SiO₂ particles were stable in air, and only gave a small weight loss from 45 to 100 °C, which could be due to water loss in Nano-SiO₂ substrate. From the curve of modified Nano-SiO₂ in Figure 3, it can be seen that the thermal degradation of modified Nano-SiO₂ occurred at 270 °C. The first weight loss (45-150 °C) indicates the loss of water molecules in polymer matrix. A sharp loss in mass was observed at 270 °C and continued to 400 °C, presumably due to a large scale of thermal degradation of KH570 chains. The char yield values were reduced by increasing the weight percentage of KH570 in the modified Nano-SiO₂. These phenomena can be

**Figure 3.** TGA thermograms of Nano-SiO₂ and modified Nano-SiO₂ with KH570.

attributed to the thermal decomposition of KH570. On the basis of these data, it can be concluded that the Nano-SiO₂ had been modified by KH570.

Particle Size and Water Contact Angle of Surface Analysis. The change in the surface of modified Nano-SiO₂ will lead to a change in dispersion in the water. Figure 4 shows the particle size analysis diagram of Nano-SiO₂-g-KH570 under different dosage of KH570. In Figure 4, with the increase of KH570 dosage, the particle size of Nano-SiO₂ and the size distribution increased and narrowed then reduced and widened, respectively. The reason of this phenomenon was that less KH570, only covers a few part of Nano-SiO₂, and the Nano-SiO₂ had played a dominant role in agglomeration. Along with the increase of KH570 dosage, the modifying agent on the surface of particle increased and self-agglomeration of particle reduced, so the average particle size decreased. When the dosage of KH570 constantly increases beyond the critical concentration, Nano-SiO₂ will be agglomerated by KH570, due to the hydrophobic association of hydrophobic chain.

Subsequently, the SL200b (contact angle measurement) was employed to study the change of water contact angle of Nano-SiO₂ before and after the modification and the results showed in Table 2. With the increase of KH570, the water contact angle had the tendency of increasing first and then decreasing (as Figure 5 showed). When the content of KH570 was 5%, the maximum water contact angle reached the peak of 79.8°. The change in the trend was the same as particle size. The reason is that the hydroxyl groups on the surface of Nano-SiO₂ are limited, and organic molecules which can be chemically

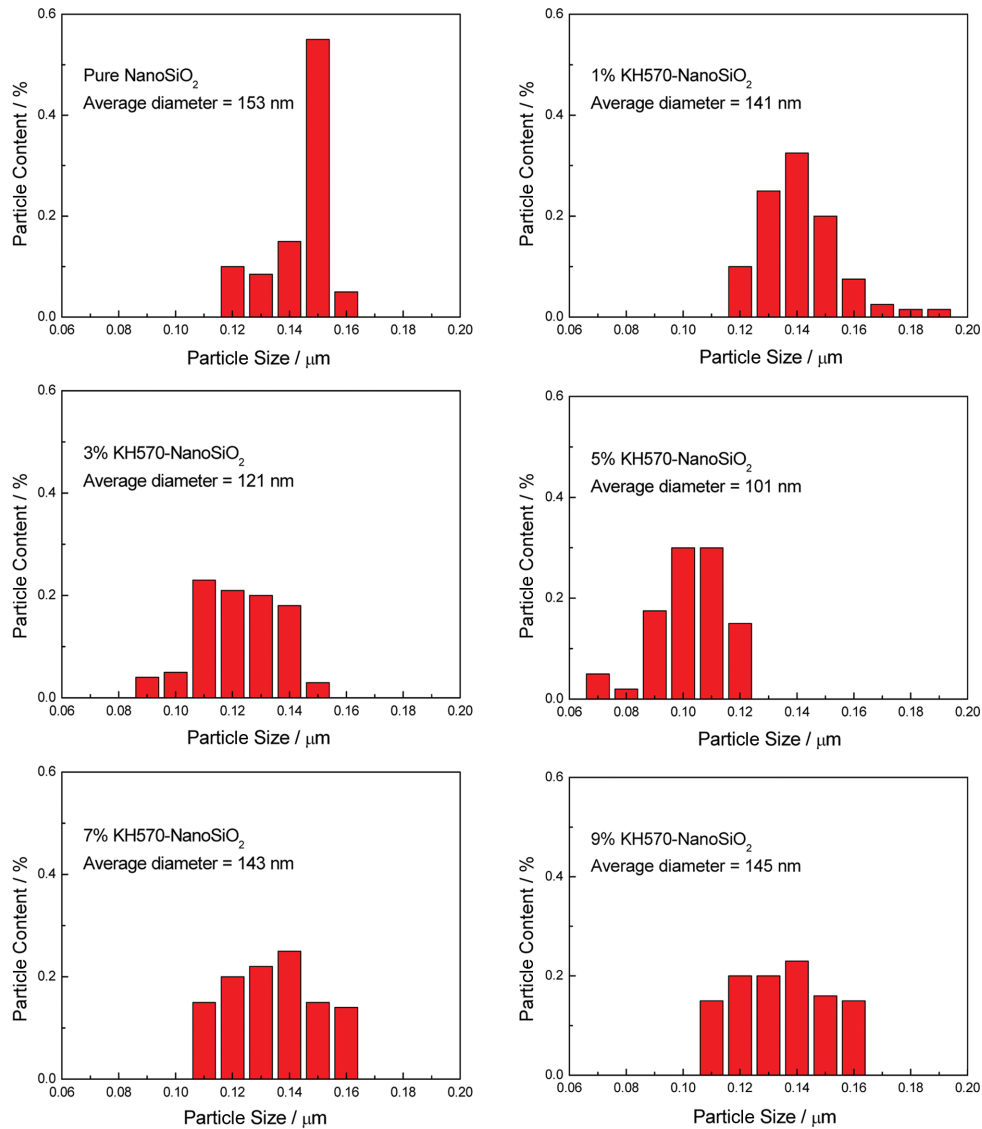


Figure 4. Influence of KH570 on the particle size and distribution of Nano-SiO₂.

Table 2. Nano-SiO₂ Surface Water Contact Angle

KH570 dosage (%)	Contact angle (°)
0	22.1
1	35.5
3	59.8
5	79.8
7	72.1
9	69.2

bonded to the particle surface are also limited. When KH570 is excessive, multilayer coating could be formed (chemical or physical bonding). Lipophilic groups of KH570 will be com-

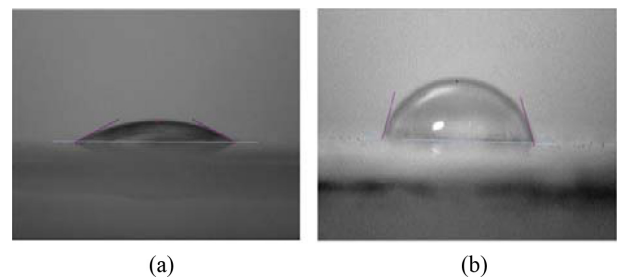


Figure 5. Nano-SiO₂ surface water contact angle. (a) unmodified Nano-SiO₂; (b) 5% KH570 modified Nano-SiO₂.

pared with each other due to hydrophobic association, and hydrophilic group stretched out, so it leads to the rebound of hydrophilic property. Meanwhile, excessive KH570 will make

Nano-SiO₂ particles gather, and this process will influence the dispersity of Nano-SiO₂.

Measure of Oil/water Interfacial Tension. The modification of Nano-SiO₂ is used in oil field development, so the interfacial tension is an important parameter. Mixing the modified Nano-SiO₂ with PS (petroleum sulfonate surfactant) results in the binary complex surfactant systems. The focus of research is the ability of reducing the interfacial tension. By using comparative analysis, the ability to reduce the interfacial tension of PS, Nano-SiO₂-PS composite system and modified Nano-SiO₂-PS composite system were shown in Figure 6.

In Figure 6, the water interfacial tension changing with time curve of PS (mass fraction was 0.5%) shows that the interfacial tension decreased rapidly at the beginning, and took about 25 min to reach 2.90×10^{-2} mN/m, then the interfacial tension declined relatively flat. More than 40 min, the interfacial tension was slightly increased. And the minimum interfacial tension of this process was 2.41×10^{-2} mN/m. The reason is that there is a “curled up” phenomenon in the interfacial tension between PS molecule and oil, which has a negative impact on the effect of flooding in the production practice.

The curve of Nano-SiO₂ and PS composite system (0.2%:0.3%) is the same as PS active water systems. There is a sharp decline in the interfacial tension at the beginning. About 25 min later, the O/W interfacial tension reached the lowest value of 2.25×10^{-2} mN/m, and then the interfacial tension remained constant with increasing time. The reason was because the intensity of the O/W interfacial film was changed with the addition of Nano-SiO₂, and it maintained the low interfacial tension at a certain time.

The changing curve of O/W interfacial tension of modified

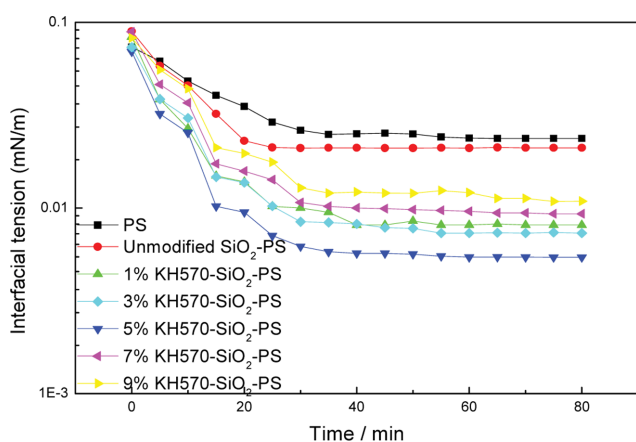


Figure 6. Nano-SiO₂-PS oil water interfacial tension ($T=72^\circ\text{C}$; $R=6000$ r/min).

Nano-SiO₂ and PS (0.2%:0.3%) composite system shows that O/W interfacial tension of this system had a rapid decline at the beginning. About 18 min later, the degradation rate slowed down. And the interfacial tension of 5% KH570-g-Nano-SiO₂-PS was the lowest (5.86×10^{-3} mN/m) after 25 min. The interfacial tension of 1% KH570-g-Nano-SiO₂-PS and 3% KH570-g-Nano-SiO₂-PS system were higher (9.3×10^{-3} and 7.33×10^{-3} mN/m). The reason was that the dosage of KH570 was too small, the organic nanoparticles surface modification could not be completed. There were a large number of hydroxyl groups on the surface, leading to a high water solubility. At the oil water interface, the nanoparticles were less. When the dosage of KH570 was high, the interfacial tension of 7% KH570-g-Nano-SiO₂-PS and 9% KH570-g-Nano-SiO₂-PS system was higher than 5% KH570-g-Nano-SiO₂-PS (8.1×10^{-3} and 1.08×10^{-2} mN/m, respectively). This is because adding excess KH570 made inadequate surface area on the Nano-SiO₂ particle for PS adsorption. Due to excessive graft, there was a low absolute value of surface ζ -potential about nanoparticles. The particles tended to agglomerate, so the system had a higher interfacial tension and poor stability.

Stability Analysis of KH570-g-Nano-SiO₂-PS System for Crude Oil Emulsion. The stability of synthetic O/W crude oil emulsion stabilized by Nano-SiO₂ systems was monitored by measuring the transmittance and backscattering of a pulsed near infrared light ($\lambda=880$ nm) with the help of Turbiscan Lab Expert manufactured by Formulacion (France). The transmittance detector receives the light, which passes through the dispersion at an angle of 180° with respect to the source, while the back scattering detector receives the light scattered backward by the dispersion at an angle of 45° . The analysis of stability was carried out as a variation of backscattering (ΔBS) profiles (Figure 7). The following formula was applied:

$$BS \approx \frac{1}{\sqrt{\lambda^*}} \quad (1)$$

where λ^* is the photon transport mean free path in the analyzed dispersion. From the physical point of view, the $\lambda^*(\varphi, d)$ value in the analyzed dispersion is evaluated by using the following formula:

$$\lambda^*(\varphi, d) = \frac{2d}{3\varphi(1-g)Q_s} \quad (2)$$

where φ is the volume fraction of particles, d is the mean diameter of particles, g and Q_s are the optical parameters given by the Mie theory.

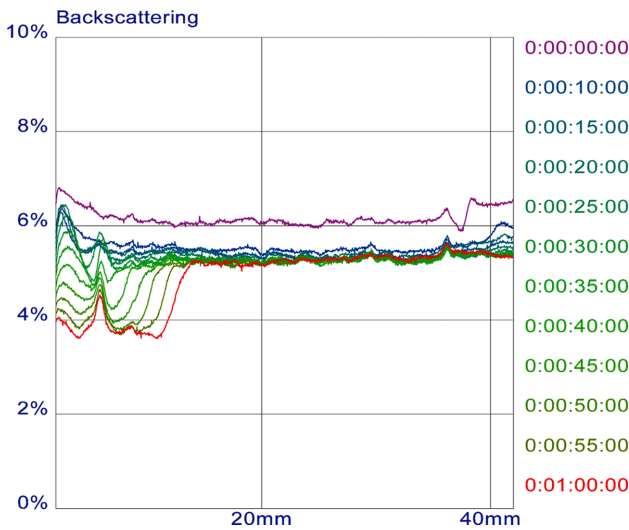


Figure 7. Backscattering profiles of O/W emulsions.

The obtained BS data was then elaborated as Δ BS profiles by the Turbiscan EasySoft Converter. The stability of emulsions can be evaluated by TSI parameter (Turbiscan Stability Index). This parameter takes into account all processes taking place in the sample (changing thickness of sediment and clear layer, process of particles settling) and the TSI value is obtained from their average. The way of calculating this coefficient is given in the following formula:

$$TSI = \sqrt{\frac{\sum_{i=1}^n (x_i - x_{BS})^2}{n-1}} \quad (3)$$

where x_i is the average backscattering for each minute of measurement, Δ BS is the average x_i , and n is numbers of scans. The higher the TSI value, the less stable the emulsion is.

As shown in Figure 8, the crude oil emulsion stability parameter of 5% KH570-g-Nano-SiO₂-PS was the minimum. At 120 min, it reached 2.15, which was the highest emulsion stability. When the amount of KH570 was too small, there was a large number of hydroxyl groups on the nanoparticle surface and the lipophilicity had changed a little. There was a large number of nanoparticles dispersing in water, so it could not be well dispersed in the O/W interface. When the KH570 dosage was too large, the KH570 was adsorbed excessively on the nanoparticle surface and it made ζ -potential of the particle surface reduce excessively. The dispersion stability of particles decreased and the stability of O/W emulsion became bad. When Nano-SiO₂ was modified by 5% KH570, the ζ -potential of the particle was moderate and agglomeration was not obvious. When PS was added into the system, PS molecules could

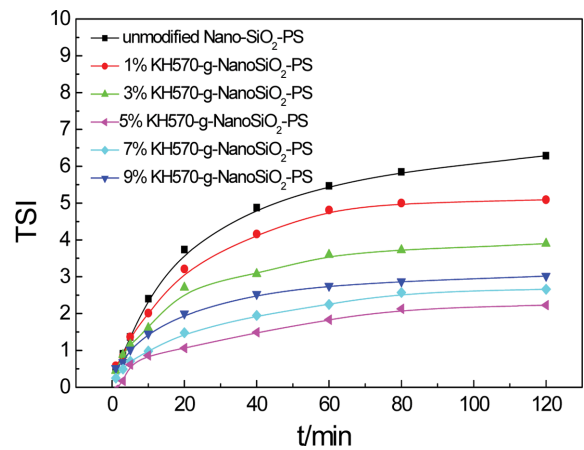


Figure 8. Crude oil emulsion TSI value change rule of KH570-g-Nano-SiO₂-PS system.

be uniformly adsorbed on the particle surface, so the system had a better oil emulsion stability.

ζ -Potential of KH570-g-Nano-SiO₂-PS System. By using ZEN3600, the ζ -potential of the different KH570-g-Nano-SiO₂-PS system was further investigated. The results were shown in Table 3. The surface ζ -potential of unmodified Nano-SiO₂-PS was -61.5 mV. The absolute value of surface ζ -potential of modified particle gradually decreased with the increase of the KH570 dosage. When the mass fraction of KH570 was 7%, the ζ -potential of particle declined significantly. When the mass fraction of KH570 was 9%, the ζ -potential was -35.8 mV. At this point, the surface of nanoparticles was coated with excess KH570, and it was difficult for PS molecules to be adsorbed on the surface of the particles. So the absolute value of ζ -potential was smaller. The electric double layer of the particle surface was thin and the agglomeration of particles was easy to occur, so the stability of the systems became bad. When the mass fraction of KH570 was small, the surface modification of Nano-SiO₂ particles was not sufficient and there were a lot of hydroxyl groups on the surface. So the absolute value of the ζ -potential was large and the agglom-

Table 3. KH570-g-Nano-SiO₂-PS System (0.2%:0.3%) Surface ζ -Potential

Combination flooding system	ζ -Potential (mV)
0% KH570-g-Nano-SiO ₂ -PS	-61.5
1% KH570-g-Nano-SiO ₂ -PS	-57.1
3% KH570-g-Nano-SiO ₂ -PS	-55.2
5% KH570-g-Nano-SiO ₂ -PS	-54.8
7% KH570-g-Nano-SiO ₂ -PS	-48.1
9% KH570-g-Nano-SiO ₂ -PS	-35.8

eration phenomenon was not obvious. Because the particles were highly hydrophilic, it was very hard to disperse in the O/W interface, and the stability of the emulsion was bad. When the mass fraction of KH570 was 5%, the surface hydroxyl groups of Nano-SiO₂ and KH570 had the best ratio of reaction. The Nano-SiO₂ particles were fully modified and the PS molecules were left with a large amount of adsorption space. In the emulsion, the ζ -potential of the particle surface was moderate, and the agglomeration phenomenon was not obvious. Due to the moderate hydrophilic-lipophilic properties, it could be well dispersed in the O/W interface, so as to stabilize the O/W emulsion.

Reducing Oil/Water Interfacial Tension Mechanism. Nano-SiO₂ particles have an ability to stabilize emulsions, which is the same as the surfactants, but the mechanism is different. The main stabilizing mechanism was shown below. The Nano-SiO₂ particles could be adsorbed in the O/W interface to form an interfacial film around the droplet. Due to the interaction of Nano-SiO₂ particles in the continuous phase, three-dimensional network structure could be formed around the emulsion droplets to stabilize the emulsion.

The process of reducing interfacial tension of the modified Nano-SiO₂-PS is much more complex than that of the surfactant. Due to the small molecular weight of the PS molecules, it could be adsorbed in the O/W interface easily. Therefore, the reduction of initial oil/water interfacial tension was due to the contribution of the PS molecules. The PS molecules were adsorbed on the surface of the nanoparticles in two ways: 1. The hydrophobic groups on PS molecule were directly adsorbed on the surface of Nano-SiO₂; 2. The hydrophobic groups were entangled with KH570 molecule, which had gone through a kind of chemical reaction with hydroxyl groups on the surface of Nano-SiO₂. Because there was a large number of PS molecules on Nano-SiO₂ particle surface, the Nano-SiO₂ particles was dragged onto the O/W interface.¹⁵ A part of the modified Nano-SiO₂ particles was wetted by the oil, and the rest was wetted by the water, which could be stably adsorbed in the O/W interface. On oil wetted part of the Nano-SiO₂ particle surface, the hydrophobic organic chains were stretched into the oil phase. Because the PS molecules were entangled with KH570, the surface hydrophobicity of Nano-SiO₂ was enhanced, and it could be dispersed well in the oil phase. The modified Nano-SiO₂-PS could be stably adsorbed in the O/W interface, as shown in Figure 9.

Because the sulfonates on PS molecule were ionized in water, there was a large number of negative charges on the

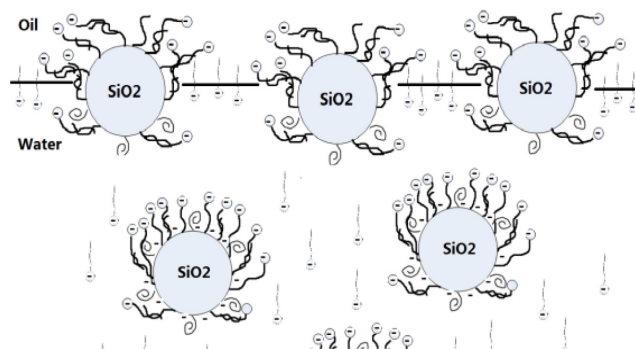


Figure 9. KH570-g-Nano-SiO₂-PS molecular diagram.

Nano-SiO₂ surface to enhance its negative surface potential. The absolute value of ζ -potential increased. Under the action of surface charge repulsion, nanoparticles were not prone to agglomeration, and they could be uniformly distributed in the O/W interface. When the KH570-g-Nano-SiO₂-PS reached saturation in the interface, the interfacial tension reached the steady state and the emulsion stability reached the highest. Because the Nano-SiO₂ particles have enhanced the mechanical properties of the O/W interfacial film more significantly, compared to the single surfactant system.

Conclusions

- (1) When the mass fraction of KH570 is 5%, the Nano-SiO₂ particles can be the best modified, because KH570 molecules can be evenly distributed on the Nano-SiO₂ particle surface and it provides adequate physical space for PS molecule adsorption.
- (2) 5% KH570-g-Nano-SiO₂-PS can decrease the O/W interfacial tension to 5.86×10^{-3} mN/m, and the interfacial tension versus time shows a linear relationship. Low interfacial tension results in the highest emulsion stability. The emulsion stability coefficient was 2.15 after 120 min.
- (3) After organic modification, the hydrophobic property of Nano-SiO₂ has greatly increased. It is beneficial for absorption in the O/W interface. The O/W interfacial film is formed by modified Nano-SiO₂ and PS (surfactant molecules). It makes the interfacial tension to reach ultra-low values and the emulsion stability has been improved.

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