**CHARACTERIZATION AND APPLICATION OF PETROLEUM SULFONATE SYNTHESIZED BY** **GAS-PHASE SO3 SULFONATION OF DISTILLATE OIL IN ROTATING PACKED BED**

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# Abstract

In this work, petroleum sulfonate (PS), which can be used for enhanced oil recovery (EOR), was synthesized by sulfonation of distillate oil using gaseous SO3 in a rotating packed bed. The content of active matter in the prepared PS reached 40.61% which was determined according to the SY/T 6424-2000 method. Also, PS was characterized by FT-IR, negative electrospray ionization fourier transform ion cyclotron resonance mass spectrometry [(−) ESI FT-ICR MS] and thermal gravimetric analysis (TGA). Results showed that the PS contains N1, O1, O2, O3, N1O2, O3S, O4S, and N1O3S classes, among which O3S, O4S, and N1O3S are the three main classes. And the chemical composition of the PS was obtained by the combined analysis of the double-bond equivalent (DBE) and carbon number (CN). TGA results showed that PS is thermally stable at the conventional reservoir temperature (<200 oC). In addition, the EOR performance of PS was studied by measuring surface tension, interfacial tension (IFT), wettability alteration and core-flooding experiments. Critical micelle concentration (CMC) of the prepared PS with a value of 0.2% was also determined by surface tension method. An ultra-low oil-water IFT value 1.327×10-3 mN/m was obtained at the CMC of PS solution. It was also found that adding PS into brine can decrease the contact angle below 90o, indicating that it can alter the rock wettability from oil-wet to water-wet surface which contributes to enhancing oil recovery. Finally, core-flooding experiments were carried out with different PS concentrations. The results showed that an additional recovery of about 30% after conventional water flooding can been obtained at a PS concentration of 0.3%. This study indicated that the PS synthesized by gas-phase SO3 sulfonation in RPB has good EOR performance, and the work is helpful for the learning of the relationship between PS composition and EOR performance and give the guidance for PS’s synthesis.

**Keywords:** Petroleum sulfonate, Chemical Composition, Rotating packed bed, Interfacial tension, Contact angle, Enhanced oil recovery

# Introduction

Nowadays, oil resources around the world are increasingly scarce, and oil companies have made great efforts to improve oil recovery to keep pace with the increased oil demand1. There are nearly 60%~70% of the crude oil remaining under the ground after primary and secondary recovery processes (water and gas flooding). Thus, the enhanced oil recovery (EOR) techniques have been developed 2,3 for the recovery of the residual oil trapped in the reservoir. Among these, chemical flooding has been widely used for the EOR process, while surfactant flooding is one of the most efficient EOR methods4-7. It can greatly reduce the oil-water interfacial tension (IFT) to ultralow value, and changes the rock’s wettability from oil-wet surface to water-wet surface in the reservoir. Therefore, types of surfactants were developed for surfactant flooding, including petroleum sulfonates (PS), alkyl benzene sulfonates, petroleum carboxylates, gemini surfactants, lignin sulfonates, etc8. PS with similar chemical structure to crude oil’s9,strong interfacial activity, thermal stability, and relatively low production cost becomes the preferred and greatly used surfactant for EOR.

PS is a complex mixture in which the alkyl chain lengths and aromatic ring contents vary in a considerable range depending on the distillate oil composition and sulfonation process. It is mainly composed of effective active matter, unsulfonated oil, inorganic salts and volatiles13. Previous studies have shown that the composition of PS has significant effect on its performance for EOR process14. Therefore, the deep understanding of the PS chemical composition from a molecular point of view is crucial for the guidance of its synthesis and application. However, the study on molecular composition analysis of PS is relatively few. In general, PS is usually characterized and quantified using high performance liquid chromatography15, mass spectrometry16, nuclear magnetic resonance spectroscopy17, ultraviolet−visible (UV−vis), and Fourier transform infrared spectroscopy (FT-IR)]18 but without a detailed chemical composition study on their active matter (AM) molecules. The above analytical methods regard the R-SO3Na as the active components of PS, where R is aromatic ring with different alkyl chains. This ambiguous definition is due to the molecular diversity of the distillate oil composition. Shi Q et al 19 have studied crude oil composition by negative electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry [(−) ESI FT-ICR MS] to identify the heteroatom compounds in crude oil. Afterwards, Rojas-Ruiz et al 20,21 and Li S et al 22 have characterized the composition of PS by means of [(−) ESI FT-ICR MS] to detect the heteroatom classes of PS. Also, the possible chemical composition of the PS was conjectured according to their characterized results. At present, limited literature elaborate on the relationship between PS composition and its application performance such as IFT reduction, wettability alteration, and recovery efficiency, and so on. Therefore, the composition of PS and the distillate oil should be characterized in detail at a molecular level for the better understanding of PS composition and its EOR performance, which are helpful for the optimization of the PS’ EOR performance via synthesis process.

Generally, PS is mainly synthesized via sulfonation of distillate with concentrated or fuming sulfuric acid, liquid sulfur trioxide, or gaseous sulfur trioxide (SO3), followed by the neutralization with sodium hydroxide or ammonia. The sulfonation process using sulfuric acid as a sulfonating agent requires high reaction temperature and high equipment costs10. While using liquid-phase SO3 as sulfonating agent is easy to over-sulfonate and form carbonization and coking for its high reactivity. In addition, solvent recovery is required in the liquid-phase SO3 process. While gas-phase SO3 sulfonation process with a lower cost and high-quality products11 has drawn the researchers’ focus. The characteristics of sulfonation process has fast reaction rate and great viscosity changes in the system, easily resulting in excessive sulfonation and easy coking which is caused by the mismatch between its fast sulfonation rate and low micro-mixing efficiency. In our previous research, it has been proved that rotating packed bed (RPB) with the advantages of short residence time, high micro-mixing and mass transfer efficiency can be used for the gas-phase SO3 sulfonation process to achieve the match between micromixing and reaction12.

In this work, PS was synthesized in the RPB via gas-phase sulfonation process. The prepared PS was characterized by FT-IR, [(−) ESI FT-ICR MS] and TGA analysis. The possible composition of the distillate oil and PS can be inferred based on the analysis of double-bond equivalent (DBE) and the carbon number (CN). Critical micelle concentration (CMC) of the prepared PS, which was determined by surface tension, was developed to explore a method to evaluate the usage of PS in EOR. In addition, the performance of PS in EOR application has been studied by measuring interfacial tension (IFT), contact angle and core-flooding experiments.

# Experimental section

## Materials

Chemical reagents such as pentane, isopropanol (IPA), sodium hydroxide (NaOH), sodium carbonate (Na2CO3) and sodium chloride (NaCl) were purchased from Aladdin Industrial (Shanghai). Table 1 shows the physical and chemical properties of the distillate oil. Saturates, aromatics, resins, and asphaltenes (SARA) compositions of the distillate oil were determined according to the reference ‘‘NB/SH/T 0509-2010 for Petroleum Asphalt Four-Component Determination Method’’. Figure 1 shows the viscosity of the distillate oil at different temperatures.

**Table 1**. Characteristics of used distillate oil for PS preparation

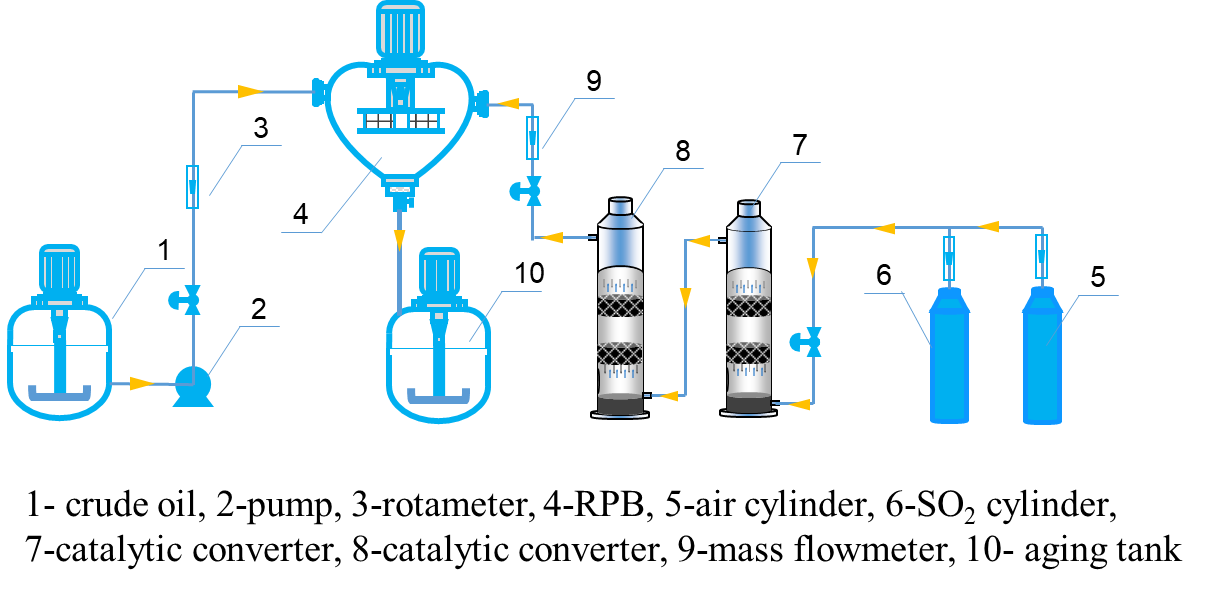
|  |  |
| --- | --- |
| parameter | distillate oil |
| density at 20 ºC (g/mL) | 0.903 |
| flash point (ºC) | 228 |
| freezing point (ºC) | -8 |
| saturates (%) | 63.8 |
| aromatics (%) | 31.6 |
| resins (%) | 4.6 |
| asphalthenes (%) | 0 |



**Figure 1.** Viscosity of distillate oil at different temperatures

## Synthesis of PS

The PS was synthesized by sulfonating the distillate oil with gaseous SO3 in the RPB. The schematic diagram of the experimental setup is shown in Figure 2.



**Figure 2.** Schematic diagram of the experimental setup

1- distillate oil tank, 2-peristaltic pump, 3-rotameter, 4-RPB, 5-air cylinder, 6-SO2 cylinder, 7,8-SO2 catalytic converter, 9-mass flowmeter, 10-aging tank

A certain amount of distillate oil was added into the stirred tank and heated to the reaction temperature of about 60 oC, then was pumped into the RPB. SO3 was generated by catalytic oxidation of SO2 gas, then entered into the RPB to react with distillate oil. The raw product discharged out of the RPB from the liquid outlet into the aging tank. After aging, the sulfonic acids were neutralized by 40% NaOH to reach the pH of 9-11, and then extracted with 50% isopropanol solution to remove unsulfonated oil. After these, the PS were concentrated by removing the isopropanol/water mixture using a rotatory evaporator. The composition of PS is listed in Table 2.

**Table 2**. Composition of the synthesized PS

|  |  |
| --- | --- |
| item | content (w%) |
| active matter | 40.61 |
| unsulfonated oil | 40.4 |
| inorganic salts | 8.72 |
| volatiles | 8.53 |

## FT-IR, TGA, and FT-ICR MS Analysis

The FT-IR Spectrometer (Perkin Elmer Spectrum GX) was used to determine the functional groups in the distillate oil and prepared PS. A thin pellet of PS and potassium bromide was prepared and used directly in FT-IR analysis. The thermal stability of the synthesized PS was studied by thermo gravimetric analyzer (Netzsch-STA 449C). The TGA analysis of synthesized PS was performed in the range of 35–620 ºC with a temperature increase rate of 5 ºC/min in nitrogen environment. FT-ICR MS analysis was performed using a Bruker Apex Ultra FT-ICR mass spectrometer equipped with a 9.4 T superconducting magnet. The sample preparation and operating procedure as well as data processing for the negative ESI FT-ICR MS analysis has been described in detail elsewhere23-25. The following equation of DBE can be used to determine the molecule elemental composition of PS (CcHhNnOoSs) 26:

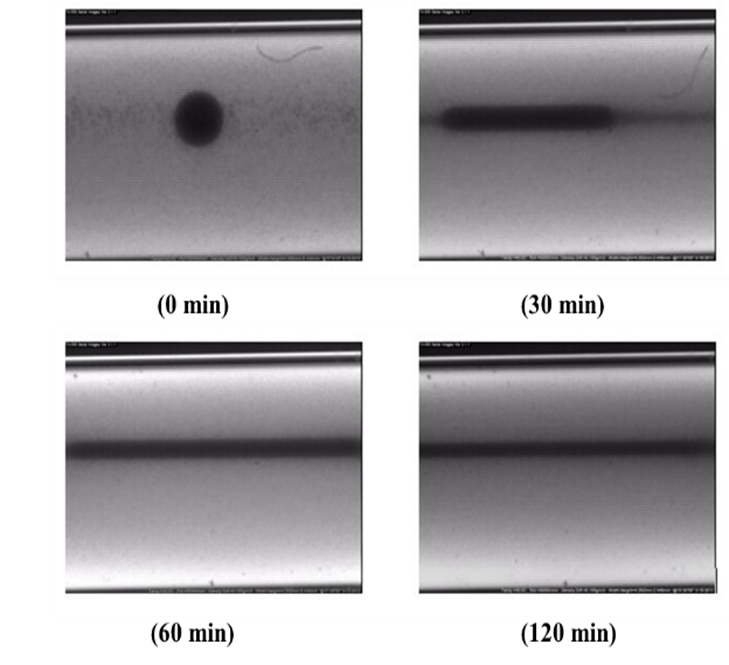
** (1)

## Surface tension and Interfacial tension measurements

Surface tension measurements were carried out in a Kruss DSA 30 Drop Shape Analyzer at a temperature of 298 K by the pendant drop method. Initially, the surface tension instrument was calibrated using deionized water and found to be obtained as 72.3 mN/m at the air-aqueous interface. Each measurement was performed at least three times to ensure results’ repeatability. The interfacial tension (IFT) between different concentrations of PS solutions and distillate oil was measured by the spinning drop technique in a TX-500C tensiometer. A drop of distillate oil was injected with a syringe into a capillary tube containing PS solution, and then rotated at a speed of 5000 rpm. The IFT was calculated by the following formula 

 (2)

where *γ* is the interfacial tension between two phases, ∆*ρ* is density difference between distillate oil and surfactant solutions, *K* is amplification factor, *L* and *D* is the length and width of oil droplet respectively, and *ω* is the angular velocity. The spinning drop tensiometer was employed for the IFT measurements, and the feature deducing of oil droplet was shown in Figure 3.

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**Figure 3.** Feature of oil droplet and diameter measurements for the IFT measurements

## Contact angle measurement

In order to study the wettability alteration of rock surface in PS solution from oil-wet to water-wet surface, the contact angle between PS solutions and oil-wet rock surface was determined using Kruss DSA 30 Drop Shape Analyzer. Contact angle values were obtained by sessile drop method with using Young-Laplace equation fitting. The rock was aged by putting it into distillate oil for two weeks at 60 °C, and then dried for 12 h.

## Flooding experiment

Flooding experiments with the PS surfactant slugs at different concentrations were carried out to evaluate the EOR efficiency of PS. The sandpack core with a length of 30 cm and a diameter of 4.5 cm was adopted for the experiments. First, the sandpack was vacuumed 4 h, then saturated brine solution was injected through the sandpack to calculate the permeability of sandpack to water (*k*w). Second, distillate oil was injected through the sandpack to calculate the connate water saturation (*S*wc), permeability of sandpack to oil (*k*o), and original oil in place (OOIP) (*S*oi). The permeability of sandpack was calculated by Darcy equation:

 (3)

where *q* is volumetric flow rate of flooding fluid (cm3/s), *A* is the total cross-sectional area of the sandpack (cm2), *μ* is the fluid viscosity (cP), d*p/*d*x* is the pressure gradient (atm/cm), and *k* is the permeability in Darcy.

Third, the brine solution was injected into the sandpack at a constant flow rate of 0.3 mL/min to displace the oil from sandpack until water-cut reached above 98%. Finally, the chemical slug was injected into the sandpack followed by water flooding. The flooding experiments were repeated using different concentrations of PS solutions to optimize the dosage of PS in EOR.

# Results and Discussion

## FT-IR Analysis

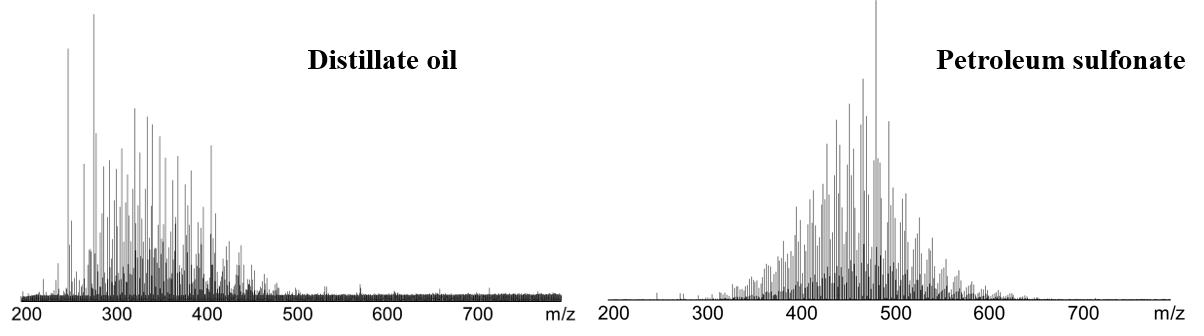
Figure 4 shows the FT-IR spectrum of the distillate oil and PS. The chemical functional groups in the distillate oil and PS were identified by the absorption peaks. The stretching vibrations peak of –OH are observed at 3443.44 cm-1. Absorption bands at 2924.22 cm-1 and 2853.54 cm-1 correspond to asymmetrical stretching vibration and symmetrical stretching vibration of CH2 respectively. The absorption bands of 1618.14 cm-1 and 1459.44 cm-1 can be assigned to the frame vibration of benzene ring, that of 1376.60 cm-1 can be attributed to the bending vibrations -CH3 group, and that of 720.51 cm-1 can be confirmed the (CH2)n, n≥4 groups. In the synthesized PS, strong absorption bands are obtained at 1128 cm-1 and 624.03 cm-1 respectively, indicating the presence of stretching vibrations of S=O and S-O bonds in sulfonate group. This indicates the sulfonation of distillate oil led to the yield of the corresponding PS.



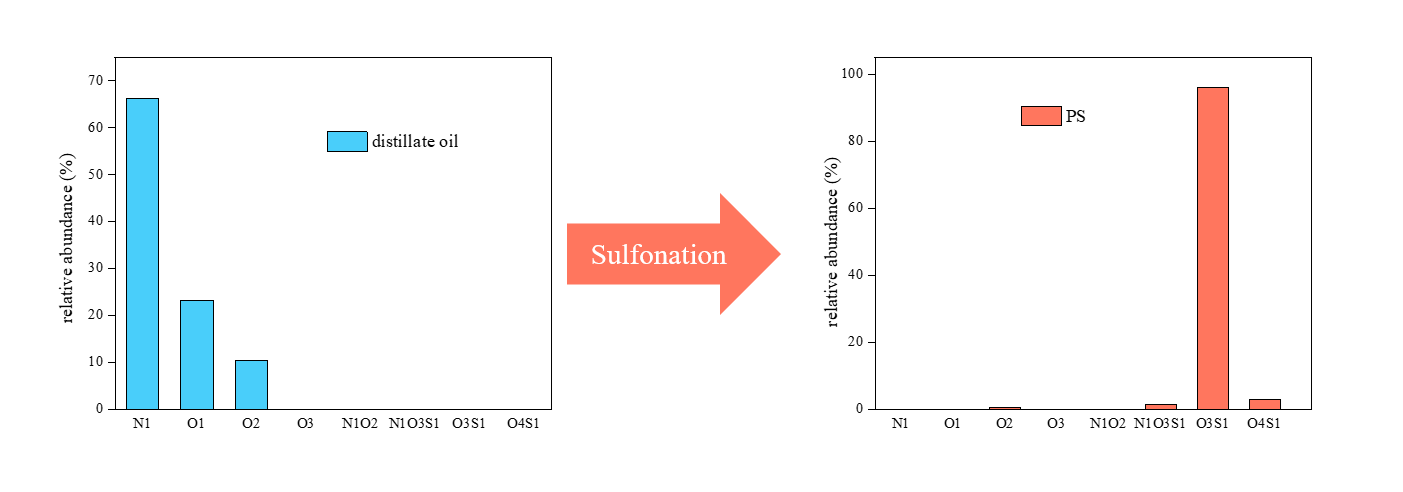
**Figure 4.** FT-IR spectra of the distillate oil and PS.

## (−) ESI FT-ICR MS Analysis

In order to investigate the chemical composition of the distillate oil and PS, the (-) ESI FT-ICR MS analysis was carried out. Figure 5 shows the (-) ESI FT-ICR mass spectra of the distillate oil and PS. It can be seen that the distribution peak of the distillate oil and PS centered at m/z 353 and 468, respectively. The distillate oil has lower mass distributions (200<m/z<500) than the PS (300<m/z<650). Results also indicate that sulfonation increases the average molecular weight of the reaction system due to the replacing of H atoms by SO3- groups.



**Figure 5**. (-) ESI FT-ICR mass spectra of the distillate oil and PS.



**Figure 6.** Classes detected by (−) ESI before and after sulfonation of distillate oil

The detected classes in the distillate oil and prepared PS are shown in Figure 6. N1, O1, and O2 are the main classes in the distillate oil. DBE and CN distributions of N1 class in the distillate oil are shown in Figure 7. The N1 class with DBE of 9 and 12 and CN of 23−26 is the most abundant compound in the distillate oil. The compounds for the N1 class with DBE value of 9 and 12 are likely carbazoles and benzocarbazoles28 respectively. The CN distributions were studied in more detail for two N series (DBE=9 and 12). Figure 7b shows that the maximum relative abundance arrives at 25 carbons for DBE=9 and 24 carbons for DBE=12, and then decreases with higher carbon numbers.



**Figure 7**. DBE versus CN distributions(a) of distillate oil‘s N1 class (b) CN distributions with DBE=9 and 12 obtained by (-) ESI FT-ICR MS.

Figure 8 shows the DBE and CN distributions of O1 and O2 classes in the distillate oil. The O1 and O2 classes which were identified by (-) ESI FT-ICR MS are phenols and carboxylic acids29-31. DBE and CN distributions for O1 class suggest that the most abundant O1 class species has DBE value of 4 and 5 and CN of 26-28. Then the relative abundance of O1 class species decreases gradually with the increase of DBE. The O2 class species with DBE of 1 are fatty acids and those with DBE of 2-7 are naphthenic acids with 1-6 naphthenic rings32. Those with higher DBE values are likely aromatic acids. The C16 and C18 with DBE of 1 should be assigned to contaminants28.

**Figure 8**. DBE and CN distributions of distillate oil’s O1 and O2 classes obtained by (-) ESI FT-ICR MS.

O3S, N1O3S1, and O4S1 classes are detected as main classes in the prepared PS, and these classes are not present in the distillate oil. This indicates that some compounds have been sulfonated. DBE and CN distributions of O3S1, N1O3S1 and O4S1 classes are shown in Figure 9. The most abundant compounds among the O3S1 class in the prepared PS are those with DBE of 4-10 and CN of 25−30, and the possible composition are listed in Table 322. In addition, amount of aromatic compounds with O and N are also sulfonated under the experimental conditions. DBE and CN distributions for O3S + N (shown in Figure 9c) indicated that the hydrophilic aromatic sulfonates were formed from nitrogen-containing aromatic compounds. DBE of 9 and 12 and CN of 25-30 are most abundant compounds, and the possible composition are listed in Table 4.







**Figure 9.** DBE and CN distributions for O3S1 (a), O4S1 (b), and N1O3S1 (c) classes of the PS obtained by (-) ESI FT-ICR MS.

**Table 3.** Possible compound for O3S1 class in the prepared PS

|  |  |  |  |
| --- | --- | --- | --- |
| DBE | type | formula | possible compound |
| 4 | Alkyl benzene | CnH2n+1—(C6H4)—SO3- |  |
| 5 | Alkyl indane | CnH2n+1—(C9H8)—SO3- |  |
| 6 | Alkyl acenaphthylene | CnH2n+1—(C12H12)—SO3- |  |
| 7 | Alkyl naphthalene | CnH2n+1—(C10H6)—SO3- |  |
| 8 | Alkyl biphenyl | CnH2n+1—(C12H8)—SO3- |  |
| 9 | Alkyl fluorene | CnH2n+1—(C13H8)—SO3- |  |
| 10 | Alkyl phenanthrene | CnH2n+1—(C14H8)—SO3- |  |

**Table 4.** Possible compound for N1O3S1 class in the prepared PS

|  |  |  |  |
| --- | --- | --- | --- |
| class | DBE | formula | Possible compound |
| N1O3S1 | 9 | CnH2n+1—(C12H6N)—SO3- |  |
| N1O3S1 | 12 | CnH2n+1—(C16H8N)—SO3- |  |

## Thermal gravimetric analysis

The thermal stability of surfactant was an important indicator while using as oil recovery chemical agent in EOR at reservoir temperature because thermal decomposition of the surfactant can reduce the oil recovery efficiency. Thermal gravimetric analysis (TGA) result of the synthesized PS is shown in Figure 10. It can be seen that the decomposition of PS occurred from 200 to 460 ºC where 47% weight loss was observed. No further weight loss was observed above 460 ºC which indicated the synthesized PS was resistant to high temperatures. For the EOR process, the conventional oil reservoir temperature remains in the range of 80-120 ºC27. For the synthesized PS, only 1.27% weight loss was observed in this temperature range, indicating that the synthesized PS with a good thermal stability can be applied in industrial oil recovery.



**Figure 10**. Thermal stability curve for the synthesized PS.

## Surface tension of PS surfactant solutions

Surface tension was measured for the determination of CMC of PS solutions. Figure 11 shows the surface tension of PS solutions at different concentrations. The surface tension decreased and then remained unchanged with an increase of the PS concentration. The concentration at which the surface tension of PS solutions attains a minimum and thereafter remains unchanged is called the CMC33. With an increase of the PS concentration, there is an increase in adsorption amount of PS at the air-water interface until the concentration reached the CMC value. At this concentration, the interface is completely adsorbed with surfactant molecules, and extra molecules are forced into the bulk phase where aggregate to form micelle structures. After CMC, the surface tension values become constant with further increase in concentration as the interface gets saturated with the surfactant monomer. In the core-flooding experiments, to obtain a maximum oil recovery efficiency, the concentration of injected PS solution should be higher than CMC to compensate for adsorption losses and recover more oil. Therefore, the determination of CMC is a preliminary test for the optimization of surfactant slugs for PS’ effective application in EOR.



**Figure 11.** Variation of surface tension with increasing PS concentration at 25ºC.

## Oil-water interfacial tension

The trapped oil can be displaced from sandpack if the oil-water interfacial tension on the surface of stone is sufficiently reduced. The earliest research dates back to 1927 when it was demonstrated that there was an inverse relationship between the oil-water interfacial tension and the oil recovery34. Afterwards, the research results showed that the efficiency of enhanced oil recovery became significant when oil-water interfacial tension fall in the range of 10-3 to 10-4 mN/m orders of magnitude 35-37. However, both PS and salt affect the oil-water interfacial tension in the EOR process. Therefore, the effect of PS concentration, salinity, and Na2CO3 concentration on the oil-water dynamic interfacial tension has been measured, as shown in Figure 12. The dynamic IFT decreased monotonically and then stabilized at the ultra-low values of 10-3 mN/m order of magnitude. There exists a dynamic equilibrium of surfactant molecules adsorption and desorption at the oil-water interface. At first, surfactant molecules diffuse from the bulk to the interface and then adsorb onto the interface, and the adsorption rate is higher than that of desorption when PS concentration is lower than CMC, leading to the decrease of dynamic IFT. When adsorption and desorption reach equilibrium, the dynamic IFT also reach stabilization38. The IFT in this system can reach the minimum of 1.327 ×10-3 mN/m at CMC. As PS concentration further increased, IFT slightly increased due to the formation of micelle structure.

The effect of salinity on dynamic IFT is shown in Figure 12b. With an increase in the salt concentration, the IFT first decreases and then increases after 3.5%. In this system, Na+ ions as counter ion were attracted by the hydrophilic group (SO3-) at the interface, and the electrostatic repulsive force between surfactant molecules is reduced. As a result, the adsorption numbers of surfactant molecules at the interface increased, resulting in the obvious decrease of IFT 39. After the optimal salinity, IFT increased due to salting-out effects which alter the distribution of surfactant molecules at the interface40.

The effect of Na2CO3 concentration on dynamic IFT is shown in Figure 12c. It can be seen that IFT with order of magnitude of 10−3 mN/m could be achieved at Na2CO3 concentration between 0.4% and 1.5%, while without Na2CO3 in the PS solutions IFT cannot reach order of magnitude of 10−3 mN/m. Alkalis can react with acidic components of crude oil to form in-situ interfacial surfactants41, which have a synergistic effect with PS molecules on IFT reduction, therefore, Na2CO3 in the EOR system is benefit for the dropping of IFT.

When PS solution is injected to the reservoir, the recovery of trapped oil in sandpack is a complicated process42. Therefore, the ultra-low IFT between crude oil and PS solution should be sustained for a sufficient time during EOR process. The effect of storage time (the prepared PS was stored at the different time at the constant temperature) on dynamic IFT is shown in Figure 12d. It can be seen that the ultra-low IFT between crude oil and PS solution (at CMC) were maintained at the order of magnitude of 10−3 mN/m for about 30 days. Which means PS solution is stable and can be used in industrial EOR process.

**Figure 12.** Effect of PS concentration (a), salinity (b), Na2CO3 concentration (c), and storage time (d) on oil-water interfacial tension.

## Contact angle measurements

Wettability, which is directly related to oil recovery efficiency, is an important indicator of PS. The rock wettability variation was studied by measuring contact angle of PS solution on rock surface. The rock has oil-wet surface while contact angle is greater than 90°, but water-wet surface while contact angle is less than 90°. Figure 13 shows that the effect of PS concentrations on the rock surface contact angle. At first, the contact angle was measured by deionized water and the value was 108.3º, indicating that the rock surface was oil-wet. The contact angle decreased and then reached a constant value of 85.6° with the passage of time. The contact angle gradually decreased to below 90° with an increase in PS concentration, showing rock surface wettability alteration from oil-wet to water-wet. The reason may be that the hydrophilic group (SO3-) adsorb onto the hydrophobic rock surface to form a water-wet layer, changing wettability to water-wet43. Standnes et al44 investigated the distribution of fluids in the core, and found that oil recovery was performed in a countercurrent flow governed by capillary force. Hence, water-wet wettability can benefit to the displacement of in rock pores and the oil recovery efficiency. In this work, using the synthesized PS can effectively alter the saturated core wettability from oil-wet to water-wet indicating the excellent oil recovery efficiency of the synthesized PS.



**Figure 13.** Effect of PS concentration on contact angle.

## Oil recovery by flooding of PS solutions

When surfactant flooding is applied in EOR, it is important to optimize the surfactant concentration to obtain maximum oil recovery efficiency at the lowest usage of PS. In general, the concentration of surfactant slug should be higher than CMC because of adsorption loss in the reservoir45. To evaluate the performance of PS, the flooding experiments were carried out with injection of different PS concentrations (from 0.3% to 0.6%). The cumulative oil recovery, water-cut percentages, and pressure differential were plotted against the pore volume of injected fluid, as shown in Figure 14. Initially, the sandpack saturated with crude oil was flooded with water, and about 37% oil was recovered after conventional water flooding. When the water-cut reached above 98%, surfactant slug was injected followed by chase water flooding till no oil can be recovered. Additional recoveries of 28.10% and 30.77% original oil in place after water injection were obtained at two different PS concentrations of 0.3% and 0.6% respectively. The additional recovery increased with an increase of PS concentration. The reduction of the oil-water interfacial tension and wettability alteration of the rock form oil-wet surface to water-oil surface in the presence of PS contributes to a higher recovery46,47. Also, the presence of polymer in the injected chemical slugs can reduce the effective permeability to water and increase the effective permeability to oil, thus improve oil mobility ratio and oil recovery efficiency48. In addition, emulsification phenomenon has been observed during the oil recovery process which is benefit for oil recovery because emulsification can improve mobility control and sweep efficiency under the reservoir conditions5.

**Figure 14.** Flooding performance of PS flooding with different concentrations: (a) 0.3% and (b) 0.6%.

# Conclusion

In this work, the PS was synthesized via gasous SO3 sulfonation in the RPB, and the chemical composition of the distillate oil and the prepared PS was characterized by means of (−) ESI FT-ICR MS analysis at the molecular level. It was found that the prepared PS with the main O3S1 sulfonated class had a high active matter of 40.61%, indicating there is no oversulfonate in the proposed synthesis process. The critical micelle concentration (CMC) value of the synthesized PS, 0.2%, were determined using surface tension method. TGA analysis showed that PS has good thermal stability in conventional reservoir temperature. An ultra-low IFT value 1.327×10-3 mN/m between the crude oil and prepared PS solution was obtained at CMC. The addition of PS obviously altered the rock surface wettability from oil-wet to water-wet, causing the obvious decrease of contact angle between the rock surface and PS solution. Core flooding experiments showed that additional oil recoveries of 28.10% and 30.77% were obtained at PS concentrations of 0.3% and 0.6% respectively after conventional water flooding. This study provides a novel route for synthesis of high EOR performance PS, and a detail research strategy for the PS composition and its EOR performance.

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