INTRODUCTION

With the rapid implementation of polymer flooding in Bohai Oilfield, the amount of produced liquid including polymer increases year by year. Usually, the polymer used in Bohai oilfield for polymer flooding is a kind of water-soluble polyacrylamides with hydrophobic long chain, named HMPAM. Due to the HMPAM is presented, the polymer-containing produced oily wastewater (PCOW) distinguishes from the normal produced oily wastewater with some unique characteristics.1-3 Firstly, it contains a large amount of degraded HMPAM. HMPAM could be subjected to heat degradation and mechanical shear during the long pass from injection well to the production well. The produced HMPAM has a shorter chain, lower molecular weight and higher degree of hydrolysis than that of injected HMPAM.4 Secondly, the residual HMPAM can work as an emulsifier at the oil-water interface. The mean size of oil droplets in PCOW usually is lower than 10 μm, which is very difficult to separate by gravity settling.5 For these characteristics, negative consequences were presented in the PCOW treatment process in offshore platform, such as the decreeing flocculation performance of the cationic flocculant (it is a kind of cationic polyacrylamide, usually named CPAM) and increasing bacteria reproduction and so on. However, the most serious problem is the

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Abstract
In this paper, a study on formation of polymer-containing oily sludge (PCOS) produced during polymer-containing oily wastewater (PCOW) treatment was carried out. First, the composition of PCOW and PCOS was compared. The results showed that not all the oil in PCOW transferred into the PCOS and the water-insoluble polymer in PCOS was the mixture of residual polymer (HMPAM) after the polymer flooding and cationic flocculant (CPAM) using for treating wastewater. Then, flocculation and zeta potential tests presented that hydrophobic water-insoluble polymer was formed by electrostatic neutralization between HMPAM and CPAM. At last, dual-polarization interferometry (DPI) tests were innovatively used to investigate the interaction between the water-insoluble polymer and oil components. The results revealed that the order of interaction between water-insoluble polymer and oil components was saturate < aromatic < resin < asphaltene. In one word, the PCOS was formed by interactions among HMPAM, CPAM and some oil components, especially the asphaltene, resin, and aromatic.

KEYWORDS
adsorption, flocculant, polymer-containing oily sludge
polymer-containing oily sludge (PCOS) could be formed and could accumulate at the top of wastewater storage tank (It is the last part in the wastewater treatment process. See the Figure S1). Taking one offshore oilfield as example, approximately 1.5-3 m³/d PCOS was generated when 2.2 × 10⁴ m³/d PCOW was treated. PCOS takes characteristics of complex, sticky, elastic and is hard to deal with. It could stick on the water treatment devices and make them disable.

Many treatment methods have been developed for sludge treatment, including high-temperature treatment, solvent extraction, biotreatment, freeze/thaw treatment, ultrasonic treatment, and thermochemical, but they make failure application in offshore oilfield due to the space and time limitation on the platform. Usually, the PCOS in offshore oilfield is picked up from the wastewater storage tanks by hand and shipped back to the land to be treated. As a result, it faces the challenges of high cost in shipping and disposing. Above all, we can find that the PCOS has a great influence on the water treatment process and the offshore oilfield production.

Although there is no good method for treating PCOS on the platform, but we can try our best to minimize the amount of PCOS. For minimizing the amount of PCOS, it is necessary to find out the formation mechanism of PCOS. In this paper, the compositions of PCOW and PCOS were analyzed firstly and then formation mechanism of the PCOS was studied by flocculation experiment and dual-polarization interferometry (DPI) analysis.

2 | EXPERIMENTS SECTION

2.1 | Material

The PCOW, PCOS, HMPAM, and CPAM were supplied by CNOOC Energy Technology Drilling & Production Co. Picture of PCOS is shown in Figure 1. The viscosity average molecular weight and the cationic degree of CPAM were 1 590 000 g/mol and 40%, respectively.

During our experiment, in order to get the similar degraded HMPAM in real PCOW, the HMPAM was degraded by ultraviolet radiation according to Ref. The viscosity average molecular weight and degree of hydrolysis of degraded HMPAM were 389 000 g/mol and 34.5%. The water used in the experiment is the synthetic brine and its composition is shown in Table 1.

2.2 | Methods

2.2.1 | Analysis of PCOW

The oil content and suspended particle content were obtained according to the Standard of China SY/T 5329-2012 “Water quality standard and practice for analysis of oilfield injecting waters in clastic reservoirs.”

HMPAM concentration was obtained by starch-cadmium iodine method according to the Standard of China SY/T 6576-2003 “Recommended practices for evaluation of polymers used in enhanced oil recovery.”

2.2.2 | Analysis of PCOS

Water content: The water content of PCOS is obtained by oven drying method. The sample which is not less than 10 g was put in 100°C oven to achieve constant weight with a glass-surface vessel.

\[
\text{Water content} = \frac{m_1 - m_2}{m} \times 100\% \quad (1)
\]

In which, \(m\) is the mass of PCOS (before dried); \(m_1\) is the total mass of PCOS (before dried) and a glass-surface vessel;

| Na⁺ | K⁺ | Mg²⁺ | Ca²⁺ | Cl⁻ | HCO₃⁻ | Total |
|-----|----|------|------|-----|-------|-------|
| 2546.07 | 32.70 | 53.90 | 149.05 | 4052.22 | 829.86 | 7663.80 |

FIGURE 1 The picture of PCOS (A) and the presence of its elastic property (B)

TABLE 1 The salinity of the synthetic water (mg/L)
Oil content: The oil was extracted by Soxhlet extraction from the dried PCOS which had been water-free. The solvent is the mixture of petroleum ether, benzene, ethanol, and chloroform (1:1:1:1, in volume). After extraction, the solvent was removed by means of a rotary evaporator and the oil was yielded.

\[
\text{Oil content} = \frac{m_3}{m} \times 100\%
\]

In which, \(m\) is the mass of PCOS (before dried); \(m_3\) is the mass of the oil.

Solid content: The solid content contains inorganics, water-soluble polymer, and water-insoluble polymer. The solid material which had been left in the chamber after Soxhlet extraction is the solid content. After baked in Muffle furnace at 550°C for 4 hours to free organics, the left material is the inorganics (\(m_4\)).

\[
\text{Inorganics content} = \frac{m_4}{m} \times 100\%
\]

In which, \(m\) is the mass of PCOS (before dried); \(m_4\) is the mass of the left material after baked in Muffle furnace at 550°C for 4 hours.

The water-soluble polymer content was get using ultrasonic cleaning for the PCOS which had been water-free and oil-free. First, the 5 g PCOS and 50 mL distilled water were added in a conical flask. Then, the conical flask was put into an ultrasonic cleaning instrument. After ultrasonic cleaning for 2 hours, the water-soluble polymer solution was collected and water-soluble polymer (\(m_5\)) was obtained by means of a rotary evaporator to remove the water.

\[
\text{Water-soluble Polymer content} = \frac{m_5}{m} \times 100\%
\]

In which, \(m\) is the mass of PCOS (before dried); \(m_5\) is the mass of the water-soluble polymer.

In addition, water-insoluble polymer content = 100% - water content - oil content - water-soluble polymer content - inorganics content.

### 2.3 | SARA Fractions

Crude oil was separated into SARA constituents, which are saturate, aromatic, resin, and asphaltene fractions according to China standard of SY/T5119-2008. The process is shown in Figure S2.

### 2.4 | The flocculation experiment

Two kinds of flocculation experiments were implemented. One kind is the flocculation between degraded HMPAM and cationic CPAM. First, prepare a solution of the 60 mg/L HMPAM; Then, 0, 50, 100, 150, 200, 250, 300, and 350 mg/L CPAM were added at room temperature, respectively; At last, the appearance of the solutions were observed.

The other kind of flocculation experiment is the flocculation between HMPAM, SARA fractions and CPAM. First, four types of the synthetic polymer-containing oily wastewater which contains 60 mg/L HMPAM and one of the SARA fractions was prepared using high speed (7000 r/min) emulsification machine at 60°C for 30 minutes (T18 digital ULTRA-TURRAX, IKA company, Germany); Then, 0, 50, 100, 150, 200, 250, 300, and 350 mg/L CPAM were added at 60°C, respectively; At last, the appearance of the solution was observed.

### 2.5 | DPI test

DPI is a label-free and surface-sensitive technique which is widely used in the solid-liquid interface to record the real-time changes of layer mass, thickness, and density. Due to the advantages of DPI, it has been applied to a variety of research areas including surfactants, protein structural changes, polyelectrolyte assemblies, biomimic biomembranes, and crystallization conditions. It is proved that DPI is a powerful and accurate method for monitoring the adsorption behaviors on the solid-liquid interface in real time. Li has used the DPI for studying the nonionic surfactant adsorption on asphaltene and polyacrylamide adsorption on resin. Wang has investigated the surfactant adsorption on fullerene grafted polymer. In this paper, DPI (Analight Nano200 Farfield Group Ltd, Crewe, UK) was firstly used to reveal the adsorptions of HMPAM and CPAM on SARA fractions. Details of experiments are as follows.

1. **Preparation of the chip:** 0.3 g SARA fraction was solved in toluene/n-heptane mixture (1:1, in volume) with the concentration of 0.3 wt% and filtered by membranes (pore size = 0.45 μm). The SARA fraction layer was then deposited on chip by Spin Coater (KW-4A, Institute of Microelectronics of Chinese Academy of Sciences) as follows: First, the solution of the SARA fraction was dropped onto the center of chip; then, the chip was spun at 1000 r/min for 60 s and a thin film was left on the surface of chip.

2. **DPI experiment:** First, NaCl solution was used to act as buffer solution to flow pass the surface of chip. Then, HMPAM and CPAM solutions were injected at speed of 25 μL/min for 900 seconds in turn. The mass after adsorption can be quantified in real time. The interaction between SARA fraction and HMPAM/CPAM was reflected by the mass adsorption.
2.6 | The other measurements

Wettability was determined by Drop shape analyzer (DSA100, Kruss GmbH, Germany). Zeta potential was determined by Nano Zeta potential meter (Malvern Instruments, UK) at 60°C. IR spectra were obtained from the Thermo Fisher Nicolet6700 FT-IR spectrometer with a KBr pellet. SEM images were performed on a FEI instrument (Quanta 450, USA).

3 | RESULTS AND DISCUSSION

3.1 | Composition analysis results of PCOW and PCOS

Tables 2 and 3 show the composition analysis results of PCOW and PCOS, respectively. Their compositions were very different. For the PCOW, the order of substance content was oil content > polymer content (HMPAM + CPAM) > inorganic suspended particle. For the PCOS, the order of substance content was polymer content > oil content > inorganics. In addition, the contents of saturate, aromatic, resin, and asphaltene in oil were 44.09 wt%, 27.77 wt%, 16.30 wt%, and 1.57 wt%, respectively.

Polymer-containing oily wastewater is the source of PCOS. PCOS was formed during the treatment of PCOW. During the treatment, oil and suspended particle in PCOW should be removed and the treated PCOW would be reinjected into the formation. By comparison of Tables 1 and 2, we can find that the mass ratio of oil to polymer of PCOW was much larger than that of PCOS. The result showed that not all the oil in PCOW transferred into the PCOS. In addition, the main solid in PCOS was the water-insoluble polymer. The polymer had two sources including HMPAM and CPAM. The results indexed that they may be separated from the water during the treatment of PCOW. IR spectra of the CPAM, HMPAM, and water-insoluble polymer in PCOS were compared to confirm this point (see Figure 2).

The peak of 1454 cm\(^{-1}\) is the characteristic absorption of COO\(^-\), which belongs to HMPAM. Peak at 1405 cm\(^{-1}\) is the stretching vibration of C-N in quaternary ammonium salt group, which belongs to CPAM. The IR analysis indicates the water-insoluble polymer possesses both the characteristic absorption peaks of CPAM and HMPAM. It confirmed that the water-insoluble polymer in PCOS is the aggregation of CPAM and HMPAM and it can precipitate from the water.

Why not all the oil in PCOW transferred into the PCOS and how water-insoluble polymer formed are related to the formation process of the PCOS. In the next context, the flocculation experiment and DPI test were done to answer these problems.

3.2 | Flocculation experiment

The appearances of HMPAM solutions after the addition of CPAM are listed in Table 4 (The photograph is shown in Figure S3). There is a trend that the turbidity of HMPAM solutions increased with CPAM concentration. At addition of 50 mg/L CPAM, the solution was clear and no precipitate settled at the bottom. At the addition of 100 mg/L CPAM, the precipitate occurred, which presented that
CPAM can destabilize the HMPAM out of the water. At the addition of 350 mg/L CPAM, the solution is not transparent and precipitate was the heaviest. Appearance observation gave us a conclusion that CPAM can destroy the stability of HMPAM in water. HMPAM and CPAM are anionic and cationic polymer, respectively, and the destroy may be caused by their electrostatic neutralization. It can be confirmed by the zeta potential (see Figure 3) experiment. As shown in Figure 3, the zeta potential of HMPAM solution increased with the addition of CPAM. Zeta potential is a key indicator of the stability of colloidal dispersions. Dispersion with higher zeta potential value (negative or positive) has higher stability. If the zeta potential value is from 0 to ±10 mV, the colloidal particles in the solution can coagulate rapidly. In one word, the result of Figure 3 confirmed that HMPAM can be separated out from the water by CPAM because of their electrostatic neutralization. As a result, the water-insoluble polymer formed during the treatment of PCOW. Figure 4 shows the SEM images of water-insoluble polymer formed by HMPAM and CPAM. We can find that it has cross-linked and porous microstructure. This structure is favorable for adsorption.

The contact angle of the water-insoluble polymer formed by CPAM and HMPAM was also measured (see Figure S4). The contact angle is 108.8°, which means it is hydrophobic. Because the water-insoluble polymer is hydrophobic, the interaction between the water-insoluble polymer and oil would be strong. The oil may adsorb on the water-insoluble polymer. Oil droplet in oily wastewater was also negative. When CPAM was added, the stability of oil droplets were also be destroyed by CPAM and flocs were formed. According to the results of Tables 1 and 2, not all the oil was transferred to be oil sludge. There are four components in oil (saturate and aromatic fractions are nonpolar component, resin and asphaltene fractions are polar component). The property of flocs formed by different oil components may be different.
Table 5 shows the property of flocs formed by different oil components (The photograph is shown Figure S5). The results presented that the flocs formed by the aromatic, resin, and asphaltene were sticky, which were similar to the oily sludge, whereas the flocs formed by saturate was not sticky and floated on the top of water.

During the flocculation test, the HMPAM was also separated from the water, which was confirmed by the decrease in CPAM addition (mg/L) 0 100 200 350

| Saturate | No flocs | No flocs | Little flocs | Flocs float on the top of water |
|---------|----------|----------|--------------|--------------------------------|
| Aromatic | No flocs | No flocs | Little flocs | Flocs attach on the beaker      |
| Resin   | No flocs | No flocs | Little flocs | Flocs attach on the beaker       |
| Asphaltene | No flocs | No flocs | Little flocs | Flocs partly float on the top and partly attach on the beaker |

During the experiment, 60 mg/L HMPAM was in the water phase.

**Figure 5** Dynamic adsorption behavior of HMPAM and CPAM on the surface of different oil components (A) saturate; (B) aromatic; (C) resin; (D) asphaltene

**Table 5** The results of flocculation tests of different oil components
HMPAM concentration (the HMPAM concentration decrease was about 95%). As a result of these investigations, it may help us to propose hypothesis that the sludge is formed by two steps. First, CPAM reacts with HMPAM and oil droplets, and the water-insoluble polymer and oil flocs were formed. Then, part of oil flocs adsorb on the surface of the water-insoluble polymer and sticky oily sludge was formed. Not all the oil flocs would adsorb on the surface of the water-insoluble polymer may due to the interactions between water-insoluble polymer (HMPAM + CPAM) and different oil components were different. The interaction difference can be investigated by DPI test.

### 3.3 DPI test

The interaction strength between different substances can be inflected by the adsorption behavior using DPI test. During the DPI test, there were two stages. The oil component was on the surface of chip and HMPAM and CPAM were injected successively. At the first stage, HMPAM flowed through the oil component surface. The adsorption mass can reflect the interaction between oil component and HMPAM. Figure 5 listed the adsorption mass. We can see that HMPAM had the largest adsorption mass on the asphaltene, which means that their interaction was the strongest. The order of interaction between HMPAM and oil components was saturate ≈ aromatic < resin < asphaltene. At the second stage, CPAM flow though the surface of HMPAM. During the second stage, water-insoluble polymer was formed. The adsorption mass of CPAM can reflect the interaction strength between oil component and the water-insoluble polymer formed by HMPAM and CPAM. The results listed in Table 6 showed that the order of interaction between water-insoluble polymer and oil components was saturate < aromatic < resin < asphaltene. According to the results of DPI test and the flocculation test of different oil components, the water-insoluble polymer could be absorbed by some oil components selectively, especially the asphaltene, resin, and aromatic. Then, PCOS was formed.

### 4 CONCLUSION

The PCOS is formed as follows: First, CPAM reacts with HMPAM and oil droplets, and the water-insoluble polymer and oil flocs were formed. Then, part of oil flocs, especially the asphaltene, resin, and aromatic, adsorbed on the surface of the water-insoluble polymer and sticky oily sludge was formed.

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**SUPPORTING INFORMATION**

Additional supporting information may be found online in the Supporting Information section at the end of the article.

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