Emulsifiers for reducing viscosity of highly viscous oil from Tahe 10 oilfield

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Abstract. The viscosity of original heavy oil increases with the decrease of temperature in the process of wellbore lifting, which makes it more difficult to lift the wellbore for Tahe 10 area reservoir, so emulsification and viscosity reduction technology is studied. The carboxymethyl polyoxyethylene alkyl alcohol ether surfactant containing different oxyethylene chains is an emulsifier with excellent tolerance of high temperature and salt. The researches indicate the compounded system of OPC-20 and DSB at 4:6 can significantly improve the solubility of OPC-20 in high-temperature brine, and it also has a good emulsification performance for Tahe heavy oil.

1. Introduction
Tahe oilfield is one of the biggest heavy oil-producing areas in China. The buried depth of the reservoir is 6000m. As the temperature decreases in the wellbore lifting process, the viscosity of heavy oil increases, making it difficult to lift the wellbore, especially in winter[1]. The salinity of the formation water in Tahe 10 is as high as 22×104 mg/L, and the content of calcium and magnesium ions is 2×104 mg/L. In addition, the fluid temperature of the viscosity reducer at the wellbore infusion point reaches 90°C (the formation temperature is 130°C). Therefore, an emulsifier suitable for heavy oil in the Tahe 10 area needs to have excellent tolerance of temperature and salt. Conventional surfactant such as alkylbenzene sulfonate, alkyl phenol polyoxyethylene cannot dissolve in Tahe formation water, not to mention their emulsification for Tahe heavy oil. The anionic surfactant with alkoxy chains in molecular can be applied in high temperature and high sanity reservoir for its tolerance of temperature and salt. Moreover, for reservoirs with different salt content, the hydrophilic-lipophilic balance of the surfactant can be adjusted by controlling the chain length of alkoxy during synthesis. So this kind of surfactant has superiority to conventional sulphonate and carboxylate surfactant when used in non-conventional reservoir. It is reported by Qiang Liu that When alkali (Na2CO3) and very dilute alkyl ether sulfate are used together, a heavy oil of 14API can be emulsified under slight interfacial disturbance[2]. These surfactants include alkyl phenol polyoxyethylene ether carboxylate, alkyl phenol polyoxyethylene ether ammonium sulfate, alkyl phenol polyoxyethylene ether hydroxypropyl sulfonate, etc[3,4]. Due to the immature industrial production technology of polyoxyethylene alkyl alcohol (or phenol) ether hydroxypropyl sulfonate, it still has problems like the degradation of polyoxyethylene alkyl alcohol (or phenol) ether sulfate salt in high-temperature water and the destruction of the structure, and other factors. In this paper, carboxymethyl polyoxyethylene alkyl
alcohol (or phenol) ether is used as viscosity reducing agent for heavy oil in the 10th district of Tahe oilfield. The hydrophilic-lipophilic balance of this type of surfactant is greatly affected by the number of oxyethylene chain segments. Therefore, the focus of the research is on the evaluation of carboxymethyl polyoxyethylene alkyl alcohol ether surfactants containing different oxyethylene chain links.

2. Experimental

2.1. Material
The carboxymethyl polyoxyethylene nonyl phenolic ether-6(OPC-6) used in the experiment is prepared by laboratory researchers by reacting alkyl phenol polyoxyethylene ether-6(OP-6, "6" means that the molecule contains 6 oxyethylene chain links.) with sodium chloroacetate. In the same way, the carboxymethyl polyoxyethylene nonyl phenolic ether-12(OPC-12, "12" means that the molecule contains 12 oxyethylene chain links.) is prepared by reacting alkyl phenol polyoxyethylene ether-12(OP-12) with sodium chloroacetate, and the carboxymethyl polyoxyethylene nonyl phenolic ether-20(OPC-20) is prepared by reacting alkyl phenol polyoxyethylene ether-20(OP-20) with sodium chloroacetate. The OP-6, OP-12 and OP-20 used in the experiment are obtained from Xingtai blue star technology. Dodecyl dimethyl hydroxy sulfobetaine (DSB) is obtained from Shanghai Nuosong industrial co., LTD. The experimental oil is taken from THK7, THK61, THK41, and THK46 in the ten districts, and the viscosity at 90°C is 1000 mPa•s, 1200 mPa•s, 1500 mPa•s, and 2200 mPa•s. The salt water used in the experiment is simulated formation water, and table 1 presents the chemical composition of the salt water.

| Ion name | Ca^{2+} | K^{+}Na^{+} | Mg^{2+} | Cl^{-} | SO_{4}^{2-} | HCO_{3}^{-} |
|---------|---------|------------|---------|-------|------------|------------|
| ρ(ion)/(mg/L) | 1159839 | 69831.7 | 1224.5 | 131489.2 | 264.3 | 145.3 |

2.2. Experimental methods

2.2.1. Evaluation of emulsifying properties of surfactants.
In the method of experimental evaluation, the mixing point of the viscosity reducing agent and the crude oil in the wellbore is first estimated. The temperature of the estimated mixing point fluid in the wellbore is about 90°C, so the heavy oil emulsification experiment is carried out at 90°C. The evaluation method is as follows:

The heavy oil and surfactant solution are mixed in a beaker at a mass ratio of 6:4. After incubating for 20 minutes in a 90°C water bath, the mixed solution is stirred with a glass rod to observe the emulsified dispersion effect of the heavy oil.

The key to viscosity reduction by emulsification is the formation of oil-in-water emulsion. Once an aqueous solution of heavy oil and surfactant can form an oil-in-water emulsion, the viscosity of the whole system will be greatly reduced. In order to quickly and effectively screen viscous oil viscosity reducers, the formation of emulsion is divided into 4 grades, which were represented by "-", "+", "++" and other symbols, as shown in table 2.

| Experimental phenomenon | The level of emulsification |
|-------------------------|-----------------------------|
| Representation symbol that crude oil does not disperse in the active agent solution | — |
| Representation symbol of crude oil dispersed in a large block shape in an active agent solution | + |
The viscosity of the formed oil-in-water emulsion is measured by using a Brookfield DVII+Pro type rotational viscometer at 6 rev/min, and calculates the viscosity reduction rate.

2.2.2. Determination of OPC-20 and OP-20 by liquid chromatography.

The mobile phase of methanol and water mixed solution (volume ratio = 9:1) is tested by using shimazu rid-10 a high performance liquid chromatograph in Japan with a flow rate of 1mL/min, column temperature of 40°C and UV detector detection system with detection wavelength of 254nm.

2.2.3. Measurement of interfacial tension.

The oil-water interfacial tension is measured by the spin drop method. The surfactant and the brine containing different degrees of salinity are configured as a solution as flooding systems. The crude oil used in the test came from the Zhuangxi oil field. The tex-500 spinning fluid interface tensiometer produced in the United States is used to test at the temperature of 90°C which is in line with the field well temperature. The width of oil droplet and its corresponding rotation speed will be recorded, and the interfacial tension will be calculated according to equation (1)

$$
\gamma = \frac{1.2336Y^3\Delta \rho}{n^3 P^2}
$$

Where Y is the droplet diameter, is the density difference between the oil displacement system and the crude oil, n is the reciprocal of the rotation speed, and P is the refractive index of the surfactant solution.

3. Results and discussion

3.1. Emulsifying Viscosity Reduction of OPC

The key to the viscosity reduction of the surfactant is the emulsification of the heavy oil into an oil-in-water emulsion while stirring. Once an oil-in-water emulsion is formed, the viscosity of the fluid is significantly reduced. Surfactant emulsification ability mainly depends on hydrophilic-lipophilic balance of surfactant and the amount of surfactant concentrations. Emulsification of heavy oil in Tahe 10 area by OPC-6, OPC-12 and OPC-20 with different mass fractions is calibrated, as shown in table 3. The test results in table 3 show that OPC-20, which contains the most oxyethylene chains in the molecules, has the best emulsification effect for the 4 kinds of heavy oils taken from THK7, THK61, THK41 and THK46. The surfactant can emulsify heavy oil at a lower mass fraction, as shown in table 4.

From the results in table 5, it can be seen that viscosity reduction rates of OPC-20 are all higher than 95% and the natural precipitation dehydration rate of the emulsion formed at 90°C is more than 90%, which basically meets the application requirements.

| Table 3. Emulsification of four heavy oils from 10-zone by OPC-6 |
|--------------------------------------------------------------|
| w(OPC-6)/% | THK7 | THK61 | THK41 | THK46 |
| 0.2 | - | - | - | - |
| 0.3 | - | + | + | + |
| 0.4 | - | + | ++ | ++ |
| 0.5 | + | + | ++ | ++ |
Table 4. Emulsification of four heavy oils from 10-zone by OPC-12

| w(OPC-12)/% | THK7 | THK61 | THK41 | THK46 |
|-------------|------|-------|-------|-------|
| 0.2         | -    | -     | +     | +     |
| 0.3         | +    | +     | ++    | ++    |
| 0.4         | +    | +     | ++    | ++    |
| 0.5         | ++   | +     | ++    | ++    |
| 0.6         | ++   | +     | +++   | +++   |
| 0.7         | ++   | +     | +++   | +++   |
| 0.8         | ++   | +     | +++   | +++   |
| 0.9         | +++  | +++   | +++   | +++   |
| 1.0         | +++  | +++   | +++   | +++   |

Table 5. Emulsification of four heavy oils from 10-zone by OPC-20

| w(OPC-20)/% | THK7 | THK61 | THK41 | THK46 |
|-------------|------|-------|-------|-------|
| 0.2         | +    | +     | ++    | +++   |
| 0.3         | ++   | +     | +++   | +++   |
| 0.4         | +++  | +++   | +++   | +++   |
| 0.5         | +++  | +++   | +++   | +++   |
| 0.6         | +++  | +++   | +++   | +++   |
| 0.7         | +++  | +++   | +++   | +++   |
| 0.8         | +++  | +++   | +++   | +++   |
| 0.9         | +++  | +++   | +++   | +++   |
| 1.0         | +++  | +++   | +++   | +++   |

3.2. Study on the Composite Emulsification Properties of OPC-20 and DSB

During the experiment, it is found that the emulsifying performance of OPC-20 significantly decreased after it is heated in Tahe simulated brine at 90°C for 10h, and the emulsifying performance of 0.5% OPC-20 for 4 kinds of heavy oil of THK7, THK61, THK41 and THK46 could only reach the "+" level. In order to investigate the reasons, four OPC-20 aqueous solutions with mass fractions of 0.25%, 0.50%, 0.75%, and 1.0% of simulated brine are heated, as shown in figure 1.
It can be seen that delamination occurs after heating the OPC-20 solution, which may be the reason why the emulsification effect of the OPC-20 aqueous solution is significantly deteriorated after long-term heat treatment. It is known from the molecular structure of OPC-20 that there are no ester bond groups in the molecule which are easily destroyed by temperature. The upper layer solution is agitated at room temperature and it is found that the precipitated material is redissolved in water. In order to clarify the composition of the precipitated substance after the heat treatment, the precipitated substance is dissolved in water and analyzed by liquid chromatography, and compared with the untreated OPC-20 and the raw material OP-20 of the synthetic OPC-20, the results are shown in figure 2.

Figure 1. The state changes of OPC-20 solution with different mass fractions before heat treatment (4 figures on the left) and after heat treatment (4 figures on the right)

It is observed that the absorption peak of OP-20 appeared at 6.4 min, and the OPC-20 without heat treatment shows two absorption peaks at 3.0 min and 6.4 min. The liquid chromatography uses a C18 silica gel column, so the stronger the polarity of the substance, the earlier the peak appears. It can be judged that the peak of the unheated OPC-20 at 6.4 min should be the unconverted raw material in the synthesis process. A small amount of OP-20 can form a mixed micelle with OPC-20, so it has better solubility in brine. In addition to the absorption peaks at 6.4 min and 3.0 min, the absorption peaks of OPC-20 after heat treatment also appear at 4.385 min. This absorption peak may be a chelate formed by OPC-20 and calcium ions or magnesium ions. The polarity of this chelate is lower than that of OPC-20 sodium salt, so its peak position lags behind that of OPC-20 sodium salt. As narrted above it can be concluded that the molecular structure of OPC-20 has not been damaged after heat treatment in Tahe simulated brine.

Figure 2. Liquid chromatographic analysis of simulated saline solution of OPC-20 before and after heat treatment

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For anionic surfactants containing oxyethylene chains, because the hydrophilic group consists of oxyethylene chains and anionic groups, its hydrophilic ability is much higher than that of non-ionic surfactants with similar molecular structures. However, in high temperature and high salinity brine, surfactants can also be separated from the brine due to the destruction of hydrogen bonds formed by oxyethylene chains and water molecules. This can explain why OPC-20 has a good emulsifying performance when heated for a short time at 90°C, but the emulsifying performance decreases significantly after a long time heating.

In 2007, Xu Jun et al. found that the resistance of carboxylate surfactants to calcium and magnesium ions was greatly improved due to the formation of mixed micelles in the solution of calcium and magnesium ions by carboxylate surfactants and DSB. Inspired by this, the researchers have compounded DSB and OPC-20 in different proportions in order to improve the solubility of OPC-20 in high temperature brine. The experimental results show that the composite system no longer appears stratification phenomenon in the high-temperature simulated brine when the proportion of DSB in the complex system is more than 60%. The results are shown in figure 3.

![Figure 3. Phase changes of OPC-20 and DSB mixed in different proportions before and after 24h heat treatment at 90°C](image)

The complex system is composed of OPC-20 and DSB in a ratio of 4:6. The oil-water interfacial tension is lower than that of 0.5% OPC-20 (the interfacial tension measured before phase separation) when the mass fraction of the system is 0.5%. The emulsification performance of the system for four kinds of heavy oil THK7, THK61, THK41 and THK46 could reach the "+++" level. The results are shown in figure 4.
Figure 4. Interfacial tension of 0.5% OPC-20 and 0.5% composite system at 90°C

4. Conclusions
- In simulated solution with salt content of $22 \times 10^4$ mg/L, carboxymethyl polyoxyethylene alkylphenol ether (OPC-20), which is a surfactant with long oxyethylene chain, has a good emulsification effect on four kinds of heavy oils in Tahe 10 area.
- The OPC-20 aqueous solution prepared by using simulated brine will be stratified when heated at 90°C for a long time, and the emulsification effect will be greatly reduced thereafter. The stratification is caused by the decrease of the solubility of OPC-20 in brine.
- The solubility of OPC-20 in high-temperature brine can be significantly improved by mixing OPC-20 with DSB in a ratio of 4:6. And the compounded system has good emulsifying property for heavy oil.

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