# Fabrication of fracturing fluid with cationic surfactants and carboxymethyl hydroxyethyl cellulose

Sanbao Dong<sup>1,2</sup> , Wen Tian<sup>1</sup>, Wenting Qiang<sup>1</sup>, Long Jiao<sup>1</sup>, Jie Zhang<sup>1</sup> , and Gang Chen<sup>1,2\*</sup>

<sup>1</sup>Shaanxi Province Key Laboratory of Environmental Pollution Control and Reservoir Protection Technology of Oilfields, Xi'an Shiyou University, Xi'an, China <sup>2</sup>Shaanxi University Engineering Research Center of Oil and Gas Field Chemistry, Xi'an Shiyou University, Xi'an, China

\*gangchen@xsyu.edu

# Abstract

The surfactant-polymer-based (S/P) fracturing fluid combines the advantages of the surfactant-based and polymer-based fracturing fluids. In this study, the synergistic tackifying of cationic surfactants and carboxymethyl hydroxyethyl cellulose and the potential application in hydraulic fracturing fluid was investigated. Firstly, cetyltrimethylammonium chloride (CTAC) and salicylic acid (SA) with a weight ratio of 4:1 were optimized as the main agent of the small molecule surfactant gel, which was then mixed with carboxymethyl 2-hydroxyethyl ether cellulose (CMHEC) and salicylic acid (SA) to obtain the S/P gel. The proppant suspension performance, gel-breaking properties, salt-resistance and thermal stability of the optimized S/P were evaluated to confirm their potential application in the hydraulic fracturing fluid. These results showed that the performance of the S/P fracturing fluid system was much better than the performance of the surfactant fracturing fluid and also the performance of polymer fracturing fluid.

Keywords: clean fracturing fluid, polymer, salicylic acid, surfactant.

**How to cite:** Dong, S., Tian, W., Qiang, W., Jiao, L., Zhang, J., & Chen, G. (2023). Fabrication of fracturing fluid with cationic surfactants and carboxymethyl hydroxyethyl cellulose. *Polímeros: Ciência e Tecnologia*, *33*(2), e20230015. https://doi.org/10.1590/0104-1428.20210010

# 1. Introduction

In recent years, with the depletion of the conventional oil and gas reservoirs, the exploration of unconventional reservoirs has attracted much attention from researchers<sup>[1]</sup>. However, the oil in the unconventional reservoirs can not be produced at an economic flow rate without the assistance from stimulation treatments<sup>[2]</sup>, which includes steam injection for heavy oil extraction, acid stimulation and hydraulic fracturing for oil recovery from low-permeability reservoirs (e.g., shale reservoirs), etc. At present, hydraulic fracturing has been considered as a common and efficient stimulation treatment to promote the exploration of the tight reservoirs<sup>[3,4]</sup>. Fracturing fluid plays a critical role in hydraulic fracturing operations, since fracturing fluid could transfer pressure, create cracks and deliver the proppant particles into the fractures during the operation<sup>[5]</sup>. The fracturing fluid is designed to have the above abilities under harsh reservoir conditions (e.g., high temperature, high salinity, etc.)<sup>[6]</sup>. Fracturing fluid based on polymers (e.g., linear polymers<sup>[7,8]</sup>, crosslinked polymers<sup>[9-12]</sup>, synthetic polymers<sup>[13-15]</sup>, etc.) have been extensively used as the working fluids during the fracturing process, since the polymer-based fracturing fluids exhibit high performances in proppant suspension, thermal stability and reducing the fluid leak-off during the fracturing stimulation<sup>[2,16]</sup>. However, the polymers in the fracturing fluids are hard to be completely broken and degraded by the breaker. The residuals with high content in the broken polymer-based fracturing fluids would block the pore throats and herein lead to formation damage<sup>[17,18]</sup>. It is reasonable to expect that a fracturing fluid with low content of polymers would result in less insoluble residuals and serious formation damage could be effectively avoided.

In order to prevent serious damage to the formation during the fracturing process, other types of fracturing fluids have been developed and employed in the fields, including viscoelastic surfactant-based<sup>[19-24]</sup> and foambased<sup>[25-31]</sup> fracturing fluid, which are selected according to the reservoir conditions. The viscoelastic surfactants (VES) can assemble into wormlike micelles (WLMs), which lead to the formation of tight networks caused by the physical association and entanglement of the WLMs<sup>[32-34]</sup>. Due to the presence of the WLMs and their entanglement, the VES fracturing fluid exhibits viscoelastic properties and excellent proppant suspension properties<sup>[33,34]</sup>. Besides, due to the low molecule weight nature of the VES, no residues are produced by the VES fracturing fluids after gel-breaking in high-temperature reservoirs and heavy damage to the proppant pack and formation can be prevented<sup>[3]</sup>. The filter cake layer on the fracture faces can not be quickly developed due to the lack of enough water-insoluble impurities in the VES fracturing fluids<sup>[2,3]</sup>. Therefore, the VES fracturing fluid would produce a large fluid leak-off into the formation.

The viscoelastic properties of the VES fracturing fluids will disappear when the fluids meet the hydrocarbons in the formation. Besides, some performances (e.g., thermal stability, proppant suspension, fluid loss, etc.) of the VES fracturing fluids can be greatly affected by the temperature and salinity conditions of the formation<sup>[35,36]</sup>. It should be noted that the high concentration of surfactants in the VES fracturing fluid increases its cost and affects its application<sup>[36]</sup>. Thus, methods need to be developed to enhance the performance of the VES fracturing fluids and enlarge their application.

Salts (e.g., KCl<sup>[37,38]</sup>, NaSal<sup>[37-39]</sup>, NaNO<sup>[40]</sup>, etc.), polymers (e.g., cellulose nanofiber<sup>[41]</sup>, hydroxypropyl guar<sup>[42]</sup>, etc.) and nanoparticles (e.g., SiO<sub>2</sub> nanoparticle<sup>[43]</sup>, ZnO nanoparticle<sup>[44]</sup>, etc.) are often used to enhance the properties (e.g., rheological property, leak-off property, filter cake-building property, etc.) of VES fracturing fluids under harsh formation conditions (e.g., high temperature, high salinity, etc.). However, while the addition of those chemicals is effective, the costs of which need to be taken into consideration. Walker et al.[45]. confirmed that the NaSal could promote the formation of worm-like micelles (WLM) at much lower concentrations of CTAB, integrate into the micelles and alter the repulsive interactions that governing the micelles, which leads to a great increase in the viscosity of the CTAB micelles. Dai et al.[46] also used the CTAB and NaSal to prepare a WLM system, which could be served as VES fracturing fluid. Besides, the cellulose derivatives, such as carboxymethyl hydroxyethylcellulose (CMHEC), have been used to viscosify the fracturing fluids<sup>[3,47-49]</sup> because of the cellulose derivatives' proper properties (easy availability, economic efficiency, low toxicity, etc.) The synergy between polymers (e.g., CMHEC) and viscoelastic surfactants has been found by many researchers in recent years<sup>[2,5,46-49]</sup>. Li et al.<sup>[47]</sup> found that the synergy appeared between CMHEC and CTAB in the construction of fracturing fluid with proper properties<sup>[46-50]</sup>.

In this paper, cetyltrimethylammonium chloride (CTAC) <sup>[51,52]</sup> and salicylic acid (SA) were used in combination with carboxymethyl 2-hydroxyethyl ether cellulose (CMHEC) to develop a S/P fracturing fluid with proper properties. The ratio of these three components of the S/P fracturing fluid was optimized through the evaluation of thermal stability, proppant suspension, gel-breaking, salt tolerance and shear stability. We expect the synergy between the surfactant (CTAC), SA and CMHEC could effectively avoid the disadvantages of the surfactant-based and the polymer-based fracturing fluids.

# 2. Experimental

#### 2.1 Materials

KCl and salicylic acid were purchased from Tianjin Shengao Chemical Reagent Co., Ltd. CaCl<sub>2</sub> (96.0% purity) was supplied from Kelong Chemical Reagent Factory in Chengdu. Salicylic acid (SA) and cetyltrimethylammonium chloride (CTAC) were purchased from Epno Chemical Co., Ltd. PVA 2488 was purchased from Hebei Shenpeng Chemical Reagent Co., Ltd Division. Polyacrylamide (PAM) was purchased from Renqiu Shangkang Chemical Co., Ltd. Carboxymethyl 2-hydroxyethyl ether cellulose (CMHEC) and carboxymethyl cellulose (CMC) were purchased from Tianjin Kemio Chemical Reagent Co., Ltd. Guar gum was purchased from Jinjia Chemical Products Co., Ltd. Gemini quaternary ammonium salt (Gemini QAS, 60% purity) was supplied from Jiangsu Jintenai Company.

## 2.2 Optimization of the ratio of CATC/SA

In this section, a series of clean fracturing fluids contain CATC and SA at weight ratios of 4:1, 5:1, 5:1, 6:1, 7:1, 8:1, 9:1 and 10:0 were prepared. In each clean fracturing fluid, the total content of CATC and SA was 2 wt%, while the content of KCl was 0.2 wt%. After the preparation of the clean fracturing fluid, the temperature resistance, the sand suspension performance and the gel-breaking properties of each fracturing fluid were investigated to find the proper ratio of CATC/SA.

## 2.3 Optimization of the ratio of CATC/SA

In this section, 0.1 wt% polymer was introduced into each clean fracturing fluid optimized in Section 2.2 to evaluate the polymer's effect on the temperature resistance, proppant suspension performance and gel-breaking properties of each S/P fracturing fluid. After these evaluations, a polymer from the candidate polymers would be selected. The optimized polymer was then introduced into the clean fracturing fluid with CTAC and SA (at an optimized CTAC/SA ratio) to obtain a series of S/P fracturing fluid. The concentration of the optimized polymer in each S/P fracturing varied from 0.1 wt% to 0.5 wt%. The apparent viscosity of each S/P fracturing fluid was evaluated at 40°C, 50°C, 60°C, 70°C and 80°C to find the optimized dosage of the optimized polymer.

#### 2.4 Thermal stability evaluation

During the fracturing operation, the viscosity of the fracturing fluid is significantly affected by the high temperature of the reservoirs. Fracturing fluid with low viscosity is not able to suspend proppants and hence no enough proppants could be placed in the fractures, leading to the formation of closed fractures after the fracturing treatment. In this section, the thermal resistance of the S/P fracturing fluid will be rated by measuring its viscosity in a temperature range of 40°C - 80°C.

#### 2.5 Proppant suspension performance test

After the hydraulic fracturing treatment, enough proppants are required to hold the fractures open to achieve an efficient conduit for the recovery of oil from formation to the wellbore. Therefore, the proppant suspension performance of the fracturing is crucial to assure the distribution of the proppant in the fractures and the success of the hydraulic fracturing. In this section, the proppant suspension performance of each fracturing fluid will be evaluated.

In each experiment, a certain amount (ranges from 5 g to 40 g) of proppant will be mixed with 100 mL fracturing fluid in a beaker. After the mixing, the beaker with fracturing fluid and proppants was kept under static conditions and placed in a water bath. The temperature of the water bath was kept at 50 °C, 60 °C, 70°C and 80 °C. The length of the time that the proppants require to sink to the bottom of

the beaker was recorded, by this way, the settling velocity of the proppants could be calculated.

#### 2.6 Gel-breaking properties evaluation

During the hydraulic fracturing treatment, the invasion of fracturing fluids into the matrix would cause the mixing of the fracturing fluids with the residual crude oil in the pores of the matrix. The solubilization of crude oil in the surfactant micelles in the fracturing fluid would lead to the decomposition of the micelles and the gel-breaking of the fracturing fluids. Besides, the mixing of fracturing fluid and oil in the presence of surfactants may also lead to the formation of an emulsion. In order to enhance the recovery of the residual oil in the formation, the emulsions formed in the pores need to be removed and flowed back to the production wells. However, this process is affected by the viscosity of the formed emulsion.

In this section, the gel-breaking properties of the fracturing were evaluated with the method described in the standard of SY/T 5107-2016 (The evaluation measurement for properties of water-based fracturing fluid). In each experiment, 400 mL S/P fracturing fluid was mixed with 5 mL crude oil and then placed in a beaker. During the whole gel-breaking time, the temperature of the fracturing fluid was measured every 30 min to monitor the gel-breaking process.

## 2.7 Salinity resistance test

After the invasion of fracturing fluids into the formation, the fluids in the formation may dilute the fracturing fluid. The salts with divalent ions in the formation water may significantly affect the performance of the fracturing fluid. In this section, CaCl<sub>2</sub> was used to evaluate the salinity resistance of the fracturing water. In each measurement, a certain amount of CaCl<sub>2</sub> (0.05 wt%, 0.1 wt%, 0.2 wt%, 0.5 wt% and 1 wt%) was introduced into the fracturing fluid. The viscosity of each fracturing fluid system at 40 °C, 50 °C, 60 °C, 70 °C and 80 °C were measured.

#### 2.8 Shear resistance performance

In this section, the viscosity of each fracturing fluid over the temperature range of 30 - 100 °C at a heating rate of 3 °C/min and a shear rate of 170 s<sup>-1</sup> was measured using a rheometer (HAAKE-pv30).

#### 3. Results and Discussions

#### 3.1 Optimization of the CTAC/SA ratio

Figure 1 shows the viscosities of the fracturing fluids with different CTAC/SA ratios. As can be seen from Figure 1, the viscosity of each fracturing fluid decreases as the ratio moves from 1:1 to 9:1, indicating that the SA's significant efficiency in increasing the viscosity of the CATC solution. It could be found that as the CTAC/ratio ranges from 1:1 to 4:1, the viscosity of the fracturing fluid at 80 °C ramps from 33 mPa·s to 66 mPa·s. However, as the CTAC/SA ratio further increases from 4:1 to 1:1, no significant increase in the viscosity value could be observed. Therefore the optimized formula of the clean fracturing fluid was measured



Figure 1. Effect of CTAC/SA ratio on the viscosity of the fracturing fluid at 80 °C.

to be 1.6 wt% CTAC and 0.4 wt% SA (CTAC/SA = 4:1) and 0.2 wt% KCl.

A possible mechanism to explain the SA's effect of viscosifing the CTAC solution (fracturing fluid) is shown in Figure 2. As presented in Figure 2, the diagram of surfactant gel formation of CTAC and SA, CTAC begins to form micelles above the critical micelle concentration, and the micelles will form a 3-D network in the presence of SA<sup>[39,45]</sup>. It should be noted that since the CTAC molecule contains the same polar group (quaternary ammonium group) with a positive charge, the electrostatic repulsions among CTAC molecules will be established if the surfactant molecules stay close. It is reasonable to expect that the repulsive force would increase the distance between two CTAC molecules, and reduce the CTAC's packing density. When SA molecules are introduced into the CTAC solution, the SA molecule with a negative charge (under alkaline conditions) could be attracted and around the CTAC molecules because of the attraction force between opposite charges. Besides, the interaction between the quaternary ammonium group of CTAC and the aromatic nucleus of the SA also contribute to the intermolecular interactions<sup>[39]</sup>. As the SA can neutralize the headgroup repulsions as described above, the SA molecules could promote the formation and growth of CTAC wormlike micelles with high CTAC packing density, thereby enhancing the viscosity of the CTAC solution.

#### 3.2 Settling velocity of the proppants in fracturing fluid

As shown in Figure 3, at each temperature, the settling velocity of the proppants increases as the proppants content increases from 5g/100mL to 40g/100mL, the settling velocity of the proppants increase as the ratio of CTAC/SA varies from 4:1 to 9:1, indicating that the SA facilitates the proppant suspending performance of the fracturing fluid, which may be due to the ability of SA in increasing the viscosity of the CTAC solution as explained in Section 3.1. The clean fracturing fluid with a CTAC/SA ratio of 4:1 is the optimized fracturing fluid. At each temperature, the settling velocity of the proppants in the fracturing fluid with 2 wt% CTAC is the highest. It can also be seen from



Figure 2. Schematic diagram of surfactant gel formation of CTAC and SA.



Figure 3. Settling velocity of proppants in different fracturing fluids.

Figure 3 that the settling velocity of the proppants increases as the temperature increases from 50 °C to 80 °C, which may be caused by the decreased viscosity of the fracturing fluid.

As shown in Figure 4, after settling for three days under static condition, the proppants remained suspended and dispersed in the fracturing fluids with various CTAC/SA ratios, indicating the well proppant suspension performance of the fracturing fluids. In Figure 4, in the fracturing fluid with a CTAC/SA ratio of 4:1, no significant bedding of the proppants is observed. While in the fracturing fluid with 2 wt% CTAC, significant bedding of the proppants can be observed. Therefore, increasing the content of SA would facilitate the suspension performance of the fracturing fluid containing CTAC, which is also caused by the SA's ability of neutralizing the positively charged ammonium group of CTAC and promoting the formation/growth of the CTAC micelles, which has been confirmed by Dai et al.<sup>[39]</sup>. and Walker et al.<sup>[45]</sup>.

#### 3.3 Settling velocity of the proppants in fracturing fluid

The gel-breaking properties are crucial for the success of the fracturing stimulation, as the fracturing fluid needs to be the fracturing fluids, the broken fracturing fluids need to be removed from the fractures and the pores of the formation to avoid the blockage of the fractures and the pores in the formation. Traditionally, the viscosity of the fracturing fluids after the breaking should be low enough to facilitate the flowing back of the broken fracturing fluids to the ground. In this section, a crude oil sample is employed as the breaker. In each experiment, a certain amount (v/v 1/80 based on the volume of the fracturing fluid) of crude oil is mixed with the fracturing fluids and then the mixtures are kept under static conditions at 80 °C. The viscosity of the mixtures is measured at 90 mins after the mixing.

broken in the wellbores and fractures. After the breaking of

Figure 5 shows the viscosities of each broken fracturing fluid at 90 mins after the mixing of fracturing fluid and crude oil. After breaking, the viscosity of fracturing fluid with CTAC and SA (with a CTAC/SA ratio of 4:1) is 1.25 mPa·s, which is the lowest viscosity. With the increase of CTAC in the broken fracturing fluids, the viscosity of which gradually increases from 1.2 mPa·s to 4.8 mPa·s, which may be caused by the emulsification of the broken fracturing fluid and crude oil



Day 3

Figure 4. The proppant suspension performance of the clean fracturing fluids at room temperature.

in the presence of CTAC during the measurement. Herein, the fracturing fluid containing CTAC and SA (with a CTAC/SA ratio of 4:1) gives superior gel-breaking properties over the other fracturing fluids.

According to the conclusions obtained above, the fracturing fluid with the CTAC/SA ratio of 4:1 exhibits the best thermal resistance, proppant suspension performance and gel-breaking property. Therefore, the optimal ratio of CTAC/SA in the surfactant fracturing fluid is 4:1. In the next section, the selection of polymers will be conducted based on this optimized CTAC/SA fracturing fluid.

# 3.4 Impacts of polymer on the thermal stability of surfactant-based fracturing fluid

In this section, 0.3 wt% polymer is introduced into the clean fracturing fluid containing 1.6 wt% CTAC and 0.4 wt% SA to see if there is synergy between the polymer and surfactant. After the preparation of each fracturing fluid containing 0.3 wt% polymer and 1.6 wt% CTAC and 0.4 wt% SA, the effects of temperature on the viscosity of each fracturing fluid is evaluated and presented in Figure 6. As can be seen from Figure 6, in the whole temperature range of 40-80 °C, the fracturing fluid containing 0.3 wt%



Figure 5. The viscosities of the broken fracturing fluids with various CTAC/SA ratios at 80 °C.

CMHEC, 1.6 wt% CTAC and 0.4 wt% SA exhibits higher thermal resistance than the fracturing fluid with 1.6 wt% CTAC and 0.4 wt% SA, indicating that there is synergy

between CMHEC and CTAC in enhancing the thermal stability of the fracturing fluid. As can be seen in Figure 7, an increase in the fraction of polymer (up to 0.5 wt%) would result in an increase in the viscosity of the fracturing fluid with 1.6 wt% CTAC and 0.4 wt% SA.

The possible interaction of cationic surfactants and CMHEC is shown in Figure 8. The cationic surfactants can absorb on the polymer and CMHEC molecules through



Figure 6. Effect of polymer on the viscosity of the surfactant-based fracturing fluid.



Figure 7. The effect of CMHEC content on the viscosity of the surfactant fracturing fluid.

hydrogen bonds. Besides, each surfactant micellar can entangle with micelles to form three-dimensional network, the polymer chains can also integrate into the networks. The entanglements between surfactant micelles and polymers can further increase the stability of networks, which can enhance the viscosity of the fracturing fluid.

## 3.5 Proppant suspension performance of the S/P fracturing fluid

Based on the above evaluation method of proppant suspension performance, the settling velocity of proppant in S/P fracturing fluid system with 0.3 wt% CMHEC, 1.6 wt% CTAC and 0.4 wt% SA is tested at 80°C, and the test results are compared with the proppant suspension performance of the fracturing fluid with 1.6 wt% CTAC and 0.4 wt% SA. As shown in Figure 9, with the increases of proppants content (from 5 wt% to 40 wt%) in the surfactant fracturing fluid, the settling speed of the proppants increases from 1.95×10<sup>4</sup> m/s to 2.31×10<sup>-4</sup> m/s. With the addition of 0.3 wt% CMHEC in the surfactant fracturing fluid, the settling speed of the proppants increases from 1.18×10<sup>-4</sup> m/s to 1.66×10<sup>-4</sup> m/s in the proppant content range of 5-40 wt%. These results indicate that the proppant suspension performance of the S/P fracturing fluid system is superior to that of the surfactant fracturing fluid, which may be due to the dense three-dimensional network structure formed by CMHEC chains and surfactant micelles, thereby increasing the viscosity of fracturing fluid.

#### 3.6 Gel-breaking properties of the S/P fracturing fluid

In this section, a certain amount (v/v 1/80 based on the volume of the fracturing fluid) of crude oil is mixed with the S/P fracturing fluids (containing 0.3 wt% CMHEC, 1.6 wt% CTAC and 0.4 wt% SA) and then the mixtures were kept under static conditions at 80 °C. The viscosity of the mixtures is recorded every 30 minutes after the mixing. The gel-breaking properties of the surfactant fracturing fluid containing 1.6 wt% CTAC and 0.4 wt% SA are evaluated with the same method. As shown in Figure 10, because the S/P fracturing fluid has a low polymer concentration, there is less residue and easy gel-breaking. The viscosity of the S/P fracturing fluid before breaking is measured to be 105 mPa·s, after being mixed with 0.125% crude oil and kept at 80 °C, the viscosity of the S/P fracturing fluid decreases quickly as the length of the breaking time increases. At 90 minutes after the addition of crude oil at 80 °C, the viscosity of the broken S/P fracturing fluid turns out to be 4.5 mPa·s,



Figure 8. The interaction of cationic surfactants and carboxymethyl hydroxyethyl cellulose.



Figure 9. Effect of CMHEC on the settling velocity of proppants.



Figure 10. Viscosity of the broken S/P fracturing fluid at 80 °C.

which indicates the low content of residuals (possibly from CMHEC) after breaking. Under the same conditions, the viscosity of the broken surfactant fracturing fluid can be decreased from 66 mPa·s to 1.25 mPa·s, which is lower than that of the broken S/P fracturing fluid. The low viscosity of the broken S/P fracturing fluid after breaking also indicates that the broken liquid could be easily cleared and brought back to the ground by the production liquids.

## 3.7 Evaluation of salinity resistance of the S/P fracturing fluid

As shown in Figure 11, without  $CaCl_2$ , the viscosity of the S/P fracturing fluid gradually decreases from 171 mPa·s to 66 mPa·s in the temperature range of 40 - 80 °C. It can also be found that a certain amount of  $CaCl_2$  could significantly affect the viscosity of the fracturing fluid. When 500 ppm  $CaCl_2$  is present in the fracturing fluid, the viscosity of the fracturing fluid can be increased up to 270 mPa·s (at 50 °C). In the temperature range of 40 - 50 °C, the viscosity ramps from 255 mPa·s to 270 mPa·s. As the temperature further increases, the viscosity of the



Figure 11. Effect of Ca2+ on the viscosity of the S/P fracturing system.

fracturing fluid gradually decreases to 202 mPa·s at 80 °C. With the presence of 1000 ppm CaCl, in the fracturing fluid, the viscosity of the fracturing fluid is higher than that of the fracturing fluid without CaCl, over the whole temperature range of 40 - 80 °C. However, it should be pointed out that, at 1000 ppm CaCl,, the viscosity of the fracturing fluid is lower than that of the fracturing fluid with 500 ppm CaCl, in the temperature range of 40-80 °C. As the concentration of the CaCl, further increases, the ability of CaCl, in increasing the viscosity of the fracturing fluid decreases. At 1000 ppm, 2000 ppm, 5000 ppm and 10000 ppm CaCl,, the maximum viscosity of each fracturing fluid is measured to be 225 mPa·s, 159 mPa·s, 120 mPa·s and 111 mPa·s, respectively. It can be shown from Figure 10 that when CaCl, is present in the fracturing fluid, the viscosity of the fracturing fluid increases and then decreases as the temperature ramps from 40 °C to 80 °C. Figure 10 implies the positive effect of CaCl, on viscosifying the fracturing fluid, which may be attributed to the introduction of Cl<sup>-</sup> ions that could reduce repulsive forces between the quaternary ammonium groups of CTAC molecules, thereby increasing the formation and growth of the wormlike micelles as described in Section 3.1.

#### 3.8 Shear resistance of the S/P fracturing fluid

Figure 12 presents the effect of shearing (with a shear rate of 170 s<sup>-1</sup>) on the viscosity of the S/P fracturing fluid as the temperature increases from 30 °C to 100 °C. As can be seen from Figure 12, at 30-50 °C, the viscosity of the S/P fracturing fluid system is relatively stable and remains above 200 mPa·s. However, as the temperature further increases, the viscosity of the S/P fracturing fluid begins to decreases. At 80 °C, the viscosity of the S/P fracturing fluid system remains higher than 100 mPa·s, indicating that the S/P fracturing fluid system has excellent thermal and shear stability, which may be due to the entanglement between polymer CMHEC chains and the CTAC wormlike micelles as described in Figure 8. The hydrogen bonds between CMHEC and CTAC may also contribute to the temperature and shear resistance of the compounded fracturing fluid system.



Figure 12. Viscosity and temperature performance of the composite fracturing fluid system after compounding.

# 4. Conclusions

In this study, a small molecule surfactant gel of CTAC and SA was formed for the potential application in the hydraulic fracturing fluid. Based on the viscosity, proppant suspension and gel breaking properties of the surfactantbased fracturing fluid, the optimized ratio of CTAC/SA is found to be 4:1. The fracturing fluid containing 1.6 wt% CTAC, 0.4 wt% SA and 0.3 wt% CMHEC gives better viscosifying and proppant suspension properties than that of the fracturing fluid containing 1.6 wt% CTAC, 0.4 wt% SA. The fracturing fluid containing 1.6 wt% CTAC, 0.4 wt% SA and 0.3 wt% CMHEC also exhibits excellent gel-breaking, Ca<sup>2+</sup> resistance and shear stability. This work will benefit the related research in hydraulic fracturing fluid preparation and crude oil production.

# 5. Author's Contribution

- Conceptualization NA.
- Data curation Wen Tian; Long Jiao.

• Formal analysis – Sanbao Dong; Wen Tian; Long Jiao; Jie Zhang.

• Funding acquisition – Gang Chen.

• Investigation – Wen Tian; Wenting Qiang; Long Jiao; Jie Zhang.

- Methodology Gang Chen.
- Project administration Gang Chen.
- Resources NA.
- Software NA.
- Supervision Wenting Qiang; Jie Zhang.
- Validation Sanbao Dong.
- Visualization NA.
- Writing original draft Sanbao Dong;
- Writing review & editing Jie Zhang; Gang Chen.

# 6. Acknowledgments

This work was financially supported by the grants from the Youth Innovation Team of Shaanxi University, Scientific Research Program Funded by Shaanxi Provincial Education Department (Program No. 21JP094) and Natural Science Basic Research Program of Shaanxi (2020JQ-775). And we thank the work of the Modern Analysis and Testing Center of Xi'an Shiyou University.

# 7. References

- Wang, J., Feng, L., Steve, M., Tang, X., Gail, T. E., & Mikael, H. (2015). China's unconventional oil: A review of its resources and outlook for long-term production. *Energy*, 82, 31-42. http:// dx.doi.org/10.1016/j.energy.2014.12.042.
- Das, A., Chauhan, G., Verma, A., Kalita, P., & Ojha, K. (2018). Rheological and breaking studies of a novel single-phase surfactant-polymeric gel system for hydraulic fracturing application. *Journal of Petroleum Science Engineering*, *167*, 559-567. http://dx.doi.org/10.1016/j.petrol.2018.04.033.
- Barati, R., & Liang, J.-T. (2014). A review of fracturing fluid systems used for hydraulic fracturing of oil and gas wells. *Journal of Applied Polymer Science*, 131(16), 40735. http:// dx.doi.org/10.1002/app.40735.
- Zhang, Y., Mao, J., Zhao, J., Yang, X., Zhang, Z., Yang, B., Zhang, W., & Zhang, H. (2018). Preparation of a novel ultrahigh temperature low-damage fracturing fluid system using dynamic crosslinking strategy. *Chemical Engineering Journal*, 354, 913-921. http://dx.doi.org/10.1016/j.cej.2018.08.021.
- Pu, W., Du, D.-J., & Liu, R. (2018). Preparation and evaluation of supramolecular fracturing fluid of hydrophobically associative polymer and viscoelastic surfactant. *Journal of Petroleum Science Engineering*, *167*, 568-576. http://dx.doi.org/10.1016/j. petrol.2018.04.032.
- Zhang, W., Mao, J., Yang, X., Zhang, H., Zhao, J., Tian, J., Lin, C., & Mao, J. (2019). Development of a sulfonic gemini zwitterionic viscoelastic surfactant with high salt tolerance for seawater-based clean fracturing fluid. *Chemical Engineering Science*, 207, 688-701. http://dx.doi.org/10.1016/j.ces.2019.06.061.
- An, M., Huang, H., Zhang, F., & Elsworth, D. (2020). Effect of slick-water fracturing fluid on the frictional properties of shale reservoir rock gouges. *Geomechanics and Geophysics for Geo-Energy and Geo-Resources*, 6(1), 28. http://dx.doi. org/10.1007/s40948-020-00153-1.
- Yang, W., Guan, B., Liang, L., Liu, X. W., & Liu, Y. (2018). Development and application of high salinity water-based fracturing fluid stabilizer. *Oilfield Chemistry*, 35(4), 622-626.
- Wang, Y., Zhang, C., Xu, N., Lan, J., Jiang, B., & Meng, L. (2021). Synthesis and properties of organoboron functionalized nanocellulose for crosslinking low polymer fracturing fluid system. *RSC Advances*, *11*(22), 13466-13474. http://dx.doi. org/10.1039/D0RA10105B. PMid:35423881.
- Zhao, M., Li, Y., Xu, Z., Wang, K., Gao, M., Lv, W., & Dai, C. (2020). Dynamic cross-linking mechanism of acid gel fracturing fluid. *Colloids and Surfaces. A, Physicochemical and Engineering Aspects*, 607, 125471. http://dx.doi.org/10.1016/j. colsurfa.2020.125471.
- Huang, Q., Liu, S., Wang, G., Wu, B., Yang, Y., & Liu, Y. (2019). Gas sorption and diffusion damages by guar-based fracturing fluid for CBM reservoirs. *Fuel*, 251, 30-44. http:// dx.doi.org/10.1016/j.fuel.2019.04.031.
- Zhang, Y., Mao, J., Xu, T., Zhang, Z., Yang, B., Mao, J., & Yang, X. (2019). Preparation of a novel fracturing fluid with good heat and shear resistance. *RSC Advances*, 9(3), 1199-1207. http://dx.doi.org/10.1039/C8RA09483G. PMid:35518047.
- Shao, Y., Mao, J., Yang, B., Zhao, J., & Yang, X. J. (2020). High performance hydrophobic associated polymer for fracturing fluids with low-dosage. *Petroleum Chemistry*, 60(2), 219-225. http://dx.doi.org/10.1134/S0965544120020115.

- 14. Tran, T., Gonzalez Perdomo, M. E., Wilk, K., Kasza, P., & Amrouch, K. (2020). Performance evaluation of synthetic and natural polymers in nitrogen foam-based fracturing fluids in the cooper basin, South Australia. *APPEA Journal*, 60(1), 227-241. http://dx.doi.org/10.1071/AJ19062.
- Tang, J., Li, H., Yan, S., & Yan, S. (2020). In situ synthesis, structure, and properties of a dendritic branched nano-thickening agent for high temperature fracturing fluid. *Journal of Applied Polymer Science*, 137(10), 48446. http://dx.doi.org/10.1002/ app.48446.
- 16. Zhao, X., Guo, J., Peng, H., Pan, R., Aliu, A. O., Lu, Q. L., & Yang, J. (2017). Synthesis and evaluation of a novel clean hydraulic fracturing fluid based on star-dendritic polymer. *Journal of Natural Gas Science and Engineering*, 43, 179-189. http://dx.doi.org/10.1016/j.jngse.2017.03.015.
- Zhao, J., Yang, B., Mao, J., Zhang, Y., Yang, X., Zhang, Z., & Shao, Y. (2018). A novel hydrophobic associative polymer by RAFT-MADIX copolymerization for fracturing fluids with high thermal stability. *Energy & Fuels*, *32*(3), 3039-3051. http://dx.doi.org/10.1021/acs.energyfuels.7b03635.
- Kang, W., Mushi, S. J., Yang, H., Wang, P., & Hou, X. (2020). Development of smart viscoelastic surfactants and its applications in fracturing fluid: A review. *Journal of Petroleum Science Engineering*, *190*, 107107. http://dx.doi.org/10.1016/j. petrol.2020.107107.
- Yan, J., Li, Y., Xie, X., Slaný, M., Dong, S., Wu, Y., & Chen, G. (2023). Research of a novel fracturing-production fluid base on small molecule surfactant. *Journal of Molecular Liquids*, 369, 120858. http://dx.doi.org/10.1016/j.molliq.2022.120858.
- Zhang, W., Mao, J., Yang, X., Zhang, H., Zhang, Z., Yang, B., Zhang, Y., & Zhao, J. (2018). Study of a novel Gemini viscoelastic surfactant with high performance in clean fracturing fluid application. *Polymers*, 10(11), 1215. http:// dx.doi.org/10.3390/polym10111215. PMid:30961140.
- Wu, Y., Zhang, J., Dong, S., Li, Y., Slaný, M., & Chen, G. (2022). Use of betaine-based gel and its potential application in enhanced oil recovery. *Gels (Basel, Switzerland)*, 8(6), 351. http://dx.doi.org/10.3390/gels8060351. PMid:35735695.
- 22. Baruah, A., Shekhawat, D. S., Pathak, A. K., & Ojha, K. (2016). Experimental investigation of rheological properties in zwitterionic-anionic mixed-surfactant based fracturing fluids. *Journal of Petroleum Science Engineering*, *146*, 340-349. http://dx.doi.org/10.1016/j.petrol.2016.05.001.
- Baruah, A., Pathak, A. K., & Ojha, K. (2016). Study on rheology and thermal stability of mixed (nonionic-anionic) surfactant based fracturing fluids. *AIChE Journal. American Institute of Chemical Engineers*, 62(6), 2177-2187. http:// dx.doi.org/10.1002/aic.15175.
- 24. Baruah, A., Pathak, A. K., & Ojha, K. (2015). Phase behavior and thermodynamic properties of lamellar liquid crystal developed for viscoelastic surfactant based fracturing fluid. *Chemical Engineering Science*, 131, 146-154. http://dx.doi. org/10.1016/j.ces.2015.03.067.
- Lv, Q., Li, Z., Li, B., Li, S., & Sun, Q. (2015). Study of nanoparticle-surfactant-stabilized foam as a fracturing fluid. *Industrial & Engineering Chemistry Research*, 54(38), 9468-9477. http://dx.doi.org/10.1021/acs.iecr.5b02197.
- Li, C., Huang, Y., Sun, X., Gao, R., Zeng, F., Tontiwachwuthikul, P., & Liang, Z. (2017). Rheological properties study of foam fracturing fluid using CO2 and surfactant. *Chemical Engineering Science*, 170, 720-730. http://dx.doi.org/10.1016/j.ces.2017.03.022.
- Yekeen, N., Padmanabhan, E., & Idris, A. K. (2018). A review of recent advances in foam-based fracturing fluid application in unconventional reservoirs. *Journal of Industrial and Engineering Chemistry*, 66, 45-71. http://dx.doi.org/10.1016/j. jiec.2018.05.039.

- Ahmed, S., Elraies, K. A., Hashmet, M. R., & Hanamertani, A. S. (2017). Viscosity models for polymer free CO2 foam fracturing fluid with the effect of surfactant concentration, salinity and shear rate. *Energies*, *10*(12), 1970. http://dx.doi. org/10.3390/en10121970.
- 29. Jing, Z., Feng, C., Wang, S., & Xu, D. (2019). Effects of temperature and pressure on rheology and heat transfer among bubbles in waterless CO2-based foam fracturing fluid. *Journal* of Natural Gas Science and Engineering, 63, 18-26. http:// dx.doi.org/10.1016/j.jngse.2019.01.005.
- Verma, A., Chauhan, G., & Ojha, K. (2018). Characterization of α-olefin sulfonate foam in presence of cosurfactants: stability, foamability and drainage kinetic study. *Journal of Molecular Liquids*, 264, 458-469. http://dx.doi.org/10.1016/j. molliq.2018.05.061.
- 31. Verma, A., Chauhan, G., Ojha, K., & Padmanabhan, E. (2019). Characterization of nano-Fe2O3-stabilized polymer-free foam fracturing fluids for unconventional gas reservoirs. *Energy & Fuels*, 33(11), 10570-10582. http://dx.doi.org/10.1021/acs. energyfuels.9b02195.
- 32. Chen, G., Yan, J., Liu, Q., Zhang, J., Li, H., Li, J., Qu, C., & Zhang, Y. (2019). Preparation and surface activity study of amino acid surfactants. *Comptes Rendus. Chimie*, 22(4), 277-282. http://dx.doi.org/10.1016/j.crci.2018.11.009.
- 33. Chen, F., Wu, Y., Wang, M., & Zha, R. (2015). Self-assembly networks of wormlike micelles and hydrophobically modified polyacrylamide with high performance in fracturing fluid application. *Colloid & Polymer Science*, 293(3), 687-697. http://dx.doi.org/10.1007/s00396-014-3454-y.
- 34. Zhang, Y., Dai, C., Qian, Y., Fan, X., Jiang, J., Wu, Y., Wu, X., Huang, Y., & Zhao, M. (2018). Rheological properties and formation dynamic filtration damage evaluation of a novel nanoparticle-enhanced VES fracturing system constructed with wormlike micelles. *Colloids and Surfaces. A, Physicochemical and Engineering Aspects*, 553, 244-252. http://dx.doi.org/10.1016/j. colsurfa.2018.05.065.
- 35. Qiu, L., Shen, Y., & Wang, C. (2018). pH- and KCl-induced formation of worm-like micelle viscoelastic fluids based on a simple tertiary amine surfactant. *Journal of Petroleum Science Engineering*, *162*, 158-165. http://dx.doi.org/10.1016/j. petrol.2017.12.037.
- 36. Yang, C., Hu, Z., Song, Z., Bai, J., Zhang, Y., Luo, J., Du, Y., & Jiang, Q. (2017). Self-assembly properties of ultra-long-chain Gemini surfactant with high performance in a fracturing fluid application. *Journal of Applied Polymer Science*, *134*(11), 44602. http://dx.doi.org/10.1002/app.44602.
- 37. Lu, Y., Yang, F., Ge, Z., Wang, S., & Wang, Q. (2015). The influence of viscoelastic surfactant fracturing fluids on gas desorption in soft seams. *Journal of Natural Gas Science and Engineering*, 27(Part 3), 1649-1656. http://dx.doi.org/10.1016/j. jngse.2015.10.031.
- Yang, M., Lu, Y., Ge, Z., Zhou, Z., Chai, C., & Zhang, L. (2020). Optimal selection of viscoelastic surfactant fracturing fluids based on influence on coal seam pores. *Advanced Powder Technology*, *31*(6), 2179-2190. http://dx.doi.org/10.1016/j. apt.2020.03.005.
- 39. Dai, C., Wu, X., Li, W., You, Q., Zhao, M., Du, M., Liu, Y., & Li, Y. (2015). The role of hydroxyethyl groups in the construction of wormlike micelles in the system of quaternary ammonium surfactant and sodium salicylate. *Soft Matter*, *11*(39), 7817-7826. http://dx.doi.org/10.1039/C5SM01698C. PMid:26314927.
- Nettesheim, F., Liberatore, M. W., Hodgdon, T. K., Wagner, N. J., Kaler, E. W., & Vethamuthu, M. (2008). Influence of nanoparticle addition on the properties of wormlike micellar

solutions. *Langmuir*, *24*(15), 7718-7726. http://dx.doi. org/10.1021/la800271m. PMid:18620438.

- 41. Gao, Z., Dai, C., Sun, X., Huang, Y., Gao, M., & Zhao, M. W. (2019). Investigation of cellulose nanofiber enhanced viscoelastic fracturing fluid system: increasing viscoelasticity and reducing filtration. *Colloids and Surfaces. A, Physicochemical and Engineering Aspects*, 582, 123938. http://dx.doi.org/10.1016/j. colsurfa.2019.123938.
- 42. Huang, F., Pu, C., Gu, X., Ye, Z., Khan, N., An, J., Wu, F., & Liu, J. (2021). Study of a low-damage efficient-imbibition fracturing fluid without flowback used for low-pressure tight reservoirs. *Energy*, 222, 119941. http://dx.doi.org/10.1016/j. energy.2021.119941.
- Wu, H., Zhou, Q., Xu, D., Sun, R., Zhang, P., Bai, B., & Kang, W. (2018). SiO2 nanoparticle-assisted low-concentration viscoelastic cationic surfactant fracturing fluid. *Journal of Molecular Liquids*, 266, 864-869. http://dx.doi.org/10.1016/j. molliq.2018.06.107.
- 44. Huang, T., & Crews, J. B. (2008). Nanotechnology applications in viscoelastic-surfactant stimulation fluids. SPE Production & Operations, 23(4), 512-517. http://dx.doi.org/10.2118/107728-PA.
- Walker, F., Isabettini, S., Kuster, S., Fischer, P., & Lutz-Bueno, V. (2019). Molecular interactions and the viscoelasticity of micellar aggregates. *Physics of Fluids*, *31*(8), 083101. http:// dx.doi.org/10.1063/1.5102110.
- 46. Dai, C., Zhang, Y., Gao, M., Li, Y., Lv, W., Wang, X., Wu, Y., & Zhao, M. (2017). The study of a novel nanoparticle-enhanced wormlike micellar system. *Nanoscale Research Letters*, *12*(1), 431. http://dx.doi.org/10.1186/s11671-017-2198-2. PMid:28673050.
- Li, G., Fang, B., Lu, Y., Li, K., Ma, M., Qiu, X., Wang, L., Liu, Y., Yang, M., & Huang, C. (2016). Intrinsic crosslingking and

gel-breaking rheo-kinetics of CMHEC/CTAB systems. *Journal of Dispersion Science and Technology*, *37*(11), 1638-1644. http://dx.doi.org/10.1080/01932691.2015.1120220.

- Aliu, A. O., Guo, J., Wang, S., & Zhao, X. ". (2016). Hydraulic fracturing fluid for gas reservoirs in petroleum engineering applications using sodium carboxy methyl cellulose as gelling agent. *Journal of Natural Gas Science and Engineering*, 32, 491-500. http://dx.doi.org/10.1016/j.jngse.2016.03.064.
- 49. Sun, R., Fang, B., Lu, Y., Qiu, X., Du, W., Han, X., Zhou, Q., & Qiu, Y. (2018). Rheological properties of hexadecyl dimethyl amine modified carboxymethyl hydroxyethyl cellulose solutions and its gelling process. *Journal of Dispersion Science and Technology*, 39(1), 138-142. http://dx.doi.org/10.1080/0193 2691.2017.1300911.
- Li, G., Fang, B., Lu, Y., Li, K., Ma, M., Yang, M., Qiu, X., Wang, L., & Liu, Y. (2016). Rheological properties and crosslinking rheo-kinetics of CMHEC/CTAB synergists systems. *Journal* of Dispersion Science and Technology, 37(12), 1826-1831. http://dx.doi.org/10.1080/01932691.2016.1142450.
- 51. Liu, Q., Gao, M., Zhao, Y., Li, J., Qu, C., Zhang, J., & Chen, G. (2020). Synthesis and interface activity of a new quaternary ammonium surfactant as an oil/gas field chemical. *Tenside, Surfactants, Detergents*, 57(1), 90-96. http://dx.doi. org/10.3139/113.110665.
- Liu, Q., Gao, M., Zhang, J., Zhang, R., Li, J., Chen, S., & Chen, G. (2020). Synthesis and interface activity of cetyltrimethylammonium benzoate. *Russian Journal of Physical Chemistry B*, *14*(1), 73-80. http://dx.doi.org/10.1134/ S1990793120010066.

Received: Mar. 05, 2021 Revised: July 25, 2021 Accepted: May 26, 2023