A Novel CO₂ Responsive Viscoelastic Surfactant based Clear Fracturing Fluid for High-Temperature Unconventional Reservoir

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Abstract. An unconventional reservoir is a term to describe a hydrocarbon resource that could not be technically or economically recoverable without stimulation. Unconventional oil and gas resources are 4-5 times over conventional oil and gas resources. Currently, there is a limitation for using slick-water volume fracturing and gas (water) injection adding energy for drainage and displacement individually. Also, the efficient hydrocarbons production from the high-temperature unconventional reservoir is the main challenge. In the current study, a CO₂ based viscoelastic surfactant fracturing fluid with a specific molar ratio of erucic acid, 2,6,10-trimethyl-2,6,10-triazaundecane, potassium hydroxide, and carbon dioxide (EA-TMTAD-KOH-CO₂) was developed as a good candidate for high-temperature and water alternating treatment for high-temperature unconventional reservoirs. The fracturing fluid will play the role of “one with multi-purpose” by proppant-carrying, CO₂ energy supplementary displacement, and surfactant imbibition drainage displacement. The fracturing fluid (EA-TMTAD-KOH-CO₂) performance evaluation method for determination of shear and heat resistance, viscoelasticity, proppant carrying capacity, gel breaking ability, and salt tolerance is employed as evaluation indices by using HTHP rheometer. The rheological results of steady shear viscosity of the fracturing fluid system confirm that the EA-TMTAD-KOH-CO₂ was observed in the properties of a wormlike micelles (WLMs) structure, micelles assembly, and the intermolecular interactions. The steady shear viscosity above 41 mPa.s at a shear rate of 170 s⁻¹ and temperature 95 °C validates the excellent proppant carrying capacity as per national industry standards of the fracturing process. Further, the gel structure breaking at temperature 135 °C and 170 s⁻¹ bear the sheare viscosity less than 5 mPa.s, which results in a rapid flow back from the well after the fracturing process. Moreover, the fluid system has high salt tolerance against different inorganic salts such as NaCl, KCl, CaCl₂, and MgCl₂ using different concentrations. By retaining the desirable qualities such as; easy to prepare, environment friendly, commercially available, high in viscoelasticity, and thermally stable; the fracturing fluid system (EA-TMTAD-KOH-CO₂) will be an outstanding candidate in industrial applications like water-alternating and high-temperature unconventional reservoirs.
1. Introduction

The hydraulic fracturing technique possesses the most essential significance in producing hydrocarbons from unconventional reservoirs. Fracturing fluid plays as the most important element during the whole fracturing process treatment [1, 2]. Fracturing fluid transport pressures to form fractures in formation and carrying proppants into the fractured formation to uphold the fracture conductivity on ideal conditions [3]. Some factors get big importance to find out the well efficiency during hydraulic fracturing jobs, such as: fracturing fluid selection, job methodology, and well turn around process [1, 4-7]. A fracturing fluid offers adequate viscosity to suspend and carrying the proppants into the fracture; and also must break into a lower viscosity fluid after completing the job [8, 9]. This property of fracturing fluid assists the fracture to clean up after allowing immediate flow back of the fluid at the well surface [1, 6, 10].

The polymer-based fluids always possess the main concern in conventional hydraulic fracturing; as the polymer residues remained within the proppant pack formation decrease the hydrocarbon production by means of the formation of filter cake on the fractures. It has been analyzed that the guar-based polymer fluids have been returned from the well about 30% to 45% during the flowback period of the fracturing process [11, 12]. Polymer residues provide considerably poor proppant pack permeability which fails in the fracture treatment effectiveness [6, 7, 13].

Efforts to remove polymer damage and to increase the effective half-length have been made completely by means of the viscoelastic surfactant (VES). VES firstly used in the Gulf of Mexico in the early 90s for the frac and pack purposes [14], since then the VES based polymer-free fluid has acquired more success in hydraulic fracturing for the oil and gas industry [1]. In recent years, VES technology has been advanced in terms of multiple evolutions in specific application requirements and also has been applied by many exploration and production companies [15, 16]. The rheological performance of VES fluid is the consequence of the 3D structure of WLMs [1]. These micelles are formed through the accumulation of surfactant molecules, where they continuously split and reattach and are almost unbreakable in a pure aqueous condition [17]. VES fluids have many advantages over conventional polymer fracturing fluid such as; simple to prepare, excellent proppant transportation ability, low treatment friction, low formation damage due to no residue, easy gel structure breaking, and involves less equipment at the well site. This VES fluid does not need polymer hydration, crosslinkers, buffers, biocides, or breakers [1, 6].

Polymer-free VES-based fluid is responsive to CO₂ and has been used with excellent results to make the fractures into formation. The VES fluid has a lower viscosity than the polymer-based fluid, yet it possesses an excellent proppant carrying ability due to the outstanding viscoelastic characteristics. After the breakup of the WLMs-based gel structure, the clean-up of the proppant pack is conducted by easy flow back of the fluid after fracturing [17]. The CO₂ compatible VES fluid system includes a combination of surfactants with particular functional groups. By adding the surfactant combination into the water, the WLMs are formed [18]. While in the presence of CO₂, different combinations of surfactants in the package will move to the interface between water and CO₂ and thus CO₂ droplets are stabilized in the aqueous media [17, 19]. All the necessary surfactants in the VES-CO₂ fluid system are packaged as a single additive.

In this study, the fracturing fluid is constructed by adding few components to water, such as; anionic surfactant (erucic acid), a functional pH buffer (potassium hydroxide), a stabilizer (2,6,10-trimethyl-2,6,10-triazaundecane), and carbon dioxide gas. When comparing to conventional fracturing, this CO₂ responsive VES based fluid system is quite simple and involves only four components instead of more than eight components. The main objective of this study is to develop a novel VES-based CO₂ responsive fracturing fluid (EA-TMTAD-KOH-CO₂), which not only fractures the reservoir but also increases the productivity with low formation damage, operational simplicity, more cost efficiency, and less environmental effects for high-temperature unconventional reservoirs.
2. Methodology

2.1. Sample preparation
CO₂ Sensitive viscoelastic clear fracturing fluid system was prepared with a designed quantity of 150 mmol erucic acid, 50 mmol TMTAD, and 300 mmol KOH with a chemical ratio of 3:1:6 respectively in deionized water (18.2 MΩ.cm) with gentle agitation at 30 °C to reach equilibrium. Under the ambient pressure of 0.1 MPa and fixed flow rate of 0.1 L/min, CO₂ bubbling brought into contact with the solution, consequently leading to a transparent viscoelastic fracturing fluid system (referred to as EA-TMTAD-KOH-CO₂), as shown in figure 1. Prior to the experiments, the prepared fracturing fluid system after CO₂ bubbling was deposited in a sealed vessel at 30 °C at least for 48 hours to prevent air contact.

2.2. Rheology Test
Rheological measurements of steady shear viscosity, thermodynamic stability, and salt tolerance of fracturing fluid system (EA-TMTAD-KOH-CO₂) were obtained as per Chinese Oil and Gas Industry Standard “SY/T 6376-2008” for general technical specifications of fracturing fluids. Rheometer Haake MARS 60 (Thermo Fisher, Germany) with a cylinder rotor (35 mm diameter with a 2º cone angle, gap size of 0.097 mm between the plate and center of the rotor) was used in the rheological study. Prior to the measurements, the samples were placed on the plate for 10 minutes at the desired temperatures to reach their stable condition.

2.3. Proppant carrying ability test
Proppant transportation ability is one of the fundamental and main properties of a fracturing fluid, which involves fracturing fluid characterization. To examine the proppant carrying capacity of the fracturing fluid system, the experiment was conducted on static conditions.

For the static proppant carrying ability test, two samples of 80-mesh proppant size with each of 15% by volume were prepared and added into the freshly prepared fracturing fluid using a glass cylinder (100 ml). After a well-stirring to ensure the good distribution of sand particles in the fracturing fluid, the settling of the proppants in the oven was monitored after every 10 minutes at a set temperature of 95 °C, while after every 40 minutes at 25 °C.

2.4. Gel breaking test
The gel structure breaking property plays an essential role in fracturing fluid, which is generally carried out after measuring the viscosity of a gel structure broken fluid [20]. Gel breaking of the fracturing fluid system “EA-TMTAD-KOH-CO₂” was achieved by the thermodynamic effect using the rheological experiment as per Chinese Oil and Gas Industry Standard “SY/T 6376-2008” for general technical specifications of fracturing fluids.
3. Results and discussions

3.1. Construction of wormlike micelles in the fluid system

A transparent viscoelastic fracturing fluid system “EA-TMTAD-KOH-CO₂” was developed at pH “9.7-10.0” after mixing and dissolving a proper quantity of erucic acid (EA), trimethyl triazaundecane (TMTAD), and potassium hydroxide (KOH) with a ratio of 3:1:6 in deionized water followed by CO₂ bubbling at specific conditions. With the bubbling of CO₂, the pH value decreased from 12.50 (water like viscous solution) to 9.97 (high viscous and gel-like solution). Figure 2 shows that the fracturing fluid system contains excellent viscosity because of the entanglement of the polymer-like WLMs induced by CO₂, which forms a transient network structure.

![Figure 2. Fracturing fluid system “EA-TMTAD-KOH-CO₂” at pH 9.97 after CO₂ bubbling](image)

3.2. Rheological performance

3.2.1. Steady shear viscosity. Steady shear viscosity as a function of the shear rate before and after bubbling of CO₂ was measured at temperature 25 °C, the results are shown in figure 3. The viscosity at pH 12.50 before CO₂ bubbling performs like Newtonian fluid behavior; correspondingly, which is normally regarded as the evidence of the absence of wormlike micelles. The viscoelastic networks appear at pH 9.97 after CO₂ bubbling and the system possesses maximum zero-shear viscosity higher than 10⁵ mPa.s. Also, the shear viscosity was increased up to about four orders of magnitude when differentiated with the viscosity at pH 12.50, which results in the shear-thinning behavior by indication of the presence of network structures composed of WLMs. The viscosity of the solutions starts to decrease after bubbling the more carbon dioxide, which means that the increase of carbon dioxide decreases the density of the molecular network. When the carbon dioxide bubbling is longer, the fluid system represents again a typical water-like Newtonian fluid behavior at pH 9.35, which is normally attributed to the spherical micelles in the fluid system.

![Figure 3. Steady shear viscosity as a function of the shear rate before and after CO₂ bubbling at 25 °C](image)
3.2.2. Thermodynamic stability. In the fracturing process, temperature and shear rate are the important elements that play a critical role in the rheological properties of WLMs-based fluid systems. The fracturing fluid viscosity and proppant carrying capacity is generally decreased at high-temperature and high shear rate. Hence, it is important to examine the thermodynamic and shear rate stability of the fracturing fluid against a high-temperature and steady shear rate. Based on this situation, Haake Mars 60 rheometer was used to measure the fluid system viscosities at different temperatures from 25 °C to 95 °C. During the test, the steady shear rate was set from 1.0 to 1000 s⁻¹, the detailed data was illustrated in figure 4. Figure 4 demonstrates that the shear viscosity has a higher value at the lowest value of temperature 25 °C. Afterward, the fluid’s viscosity decreased gradually by increasing the temperature; and the lower value of viscosity at 1000 s⁻¹ shear rate remains 29.48 mPa.s at 95 °C. According to the China national standards for fracturing fluids, the fluid viscosity to hold the proppants should be greater than 20 mPa.s at the shear rate of 170 s⁻¹. As per this phenomenon, this fluid system holds the viscosity value of 41 mPa.s at a temperature of 95 °C, which is sufficient to build good fracturing operations.

![Figure 4. Shear viscosity of fluid system at different temperatures and steady shear rate](image)

3.2.3. Proppant carrying capacity. Proppants suspension and transportation play a very crucial role by helping the fracturing fluid to carry the proppants to the wellbore and into the fractured formation. If the proppant-carrying ability is poor, then the rapid settlement of the proppants into the fractures will lead to severe accidents such as plugging. The proppant carrying capacity test was conducted by visual observation of proppant fall. Two samples of solution were prepared for measuring the proppants settling height at 25 °C and 95 °C. Proppants of 80 mesh with 15% by volume were added in the 100 ml fluid system in a glass cylinder and then stirred to ensure the proppant must be well-distributed in the solution. The settling height of proppants at 25 °C was measured after every 40 minutes, while at 95 °C was recorded every 10 minutes. The complete illustration of the experiment is shown in figure 5, while the details of proppants settling heights are mentioned in table 1. It was observed in the experiment that no sedimentation occurred during the test at 25 °C up to four hours; while at 95 °C, the proppants were completely settled down in 70 minutes. It was analyzed from the results at 25 °C that the fracturing fluid “EA-TMTAD-KOH-CO₂” possesses an excellent viscoelastic behavior because of highly strengthened WLMs. Further, the sedimentation within 70 minutes at 95 °C showed a decrease in viscoelasticity due to the destruction of molecular structure and by removal of CO₂. Hence, the results authenticate that the fracturing fluid at 95 °C is applicable to transport the proppants into the well for fracturing purposes.
Figure 5. The proppant carrying capacity of the fluid system at different temperatures

Table 1. Detail of proppants settling height with respect to time at different temperatures

| Settling Time, min | Settling Height, cm | Settling Time, min | Settling Height, cm |
|-------------------|---------------------|-------------------|---------------------|
| 0                 | 0                   | 0                 | 0                   |
| 40                | 0                   | 10                | 0.4                 |
| 80                | 0                   | 20                | 2.3                 |
| 120               | 0                   | 30                | 4.2                 |
| 160               | 0                   | 40                | 7.9                 |
| 200               | 0                   | 50                | 11.3                |
| 240               | 0                   | 60                | 14.7                |
|                   |                     | 70                | 15.0                |

3.2.4. Gel breaking property. Gel breaking is also another important property of fracturing fluid that is mostly performed by the viscosity of breaking liquid. If the fracturing fluid does not break quickly and thoroughly after construction, then it will be very hard to flow back and which results in the formation of residue into the fractures and pores. The formed residue causes serious formation damage by means of reducing the permeability damage to the reservoir. To avoid such kind of situation, a gel breaking test was conducted to measure the shear viscosity at a shear rate of 170 s\(^{-1}\) in three intervals of time and temperature, as shown in figure 6. During the first-time interval, viscosity was measured between the temperature of 25 °C and 135 °C. Viscosity decreased rapidly with an increase in temperature because the increasing temperature leads to a decrease in the solubility of CO\(_2\) in the fracturing fluid, which results in the breakdown of the molecular structure. When the temperature reached 135 °C, then the temperature was kept constant for measuring the viscosity during the second-time interval of 3600 seconds. The viscosity remained less than 5 mPa.s like water during the whole time of the second-time interval at 135 °C, which indicated that the CO\(_2\) was completely removed out from the fluid system. The third time interval was set to cool down the fluid system again at 25 °C. While cooling down the temperature from 135 °C to 25 °C, the viscosity remained between 10 and 11 mPa.s, which showed a typical Newtonian fluid behavior like water. As the liquid gel breaking viscosity must be less than 5 mPa.s at a shear rate 170 s\(^{-1}\) according to the Chinese Oil and Gas Industry Standard “SY/T 6376-2008” for general technical specifications of fracturing fluids, so the results indicated clearly that the gel structure of this fluid system was easily broken down by heating at a temperature of 135 °C.
3.2.5. Salt tolerance. A high amount of salt concentration in the formation water often causes to decline in the oil recovery in terms to increase the formation damage and imposes a poor effect on the performance of fracturing fluids. Hence it is essential to study the consequence of monovalent and divalent salt ions on the rheological performance of the CO₂ responsive clear fracturing fluid. To investigate this study, inorganic salts such as NaCl, KCl, CaCl₂, and MgCl₂ were added using different concentrations in the EA-TMTAD-KOH-CO₂ fluid system to examine the salinity effect on the viscosity of the fluid system. The apparent viscosities of the fracturing fluid system at different concentrations of monovalent salts (NaCl, KCl), and divalent salts (CaCl₂ and MgCl₂) were measured at 25 ºC, the results are depicted in figures 7a and 7b, respectively. The influence of salt concentration on fluid viscosity was investigated at a shear rate from 0.1 to 1000 s⁻¹. The apparent viscosity was a little bit increased when the concentration of different salts was at a lower value. Similarly, the fluid system viscosity was also increased by adding a higher concentration of salts. The increase in viscosity can be recognized as the addition of salt, which protects the electrostatic repulsion between the surfactant polar head base and therefore upholds the growth of the WLMs [21]. Thus, the results from the analysis indicate that the fracturing fluid system (EA-TMTAD-KOH-CO₂) bears a good salinity tolerance and does not disrupt the network structure of VES fluids.

**Figure 6.** Shear viscosity and temperature as a function of time, before and after gel breaking, shear rate 170 s⁻¹

**Figure 7a.** Effect of monovalent salt ions on shear viscosity of fluid system at 25 ºC

**Figure 7b.** Effect of divalent salt ions on shear viscosity of fluid system at 25 ºC
4. Conclusions
In summary, the WLMs-based fluid system "EA-TMTAD-KOH-CO₂" was developed by simply mixing erucic acid, 2,6,10-trimethyl-2,6,10-triazadecane, and potassium hydroxide with a molar ratio of 3:1:6, followed by CO₂ bubbling. Results from the extensive experiments show that the fracturing fluid "EA-TMTAD-KOH-CO₂" bears an excellent shear viscosity, good thermodynamic stability, thermal-based gel breaking ability, and high salt tolerance. The reasonable gel-like viscoelastic feature of micelles assembly with excellent viscosity higher than 10⁵ mPa.s at 25 °C and heat resistance at 95 °C indicate that the fracturing fluid system is a good candidate to suspend and transport the proppant during fracturing job. Also, the high salt resistance with no reasonable change in the shear viscosity, and the gel structure breaking at 135 °C promotes the rapid flow back of the fluid from the well after the fracturing job, which indicates that the fluid system is formation and fracture friendly with a feature of no formation damage in high salinity and high-temperature reservoirs.

The CO₂ responsive viscoelastic surfactant based clear fracturing fluid will be a good candidate for the water-alternating CO₂ flooding enhanced oil recovery in unconventional high-temperature reservoirs by considering the operational simplicity, commercially availability, environment friendliness, and excellent rheological features.

References
[1] Samuel M M, Card R, Nelson E B, Brown J E, Vinod P S, Temple H L, Qu Q and Fu D K 1999. Polymer-free fluid for fracturing applications. SPE Drilling & Completion 14(04) 240-246
[2] Zhao G, Dai C, Wang S, and Zhao M 2015 Synthesis and application of nonionic polyacrylamide with controlled molecular weight for fracturing in low permeability oil reservoirs Journal of Applied Polymer Science, 132(11)
[3] Zhang J, Zhang M, Zhang S, Bai B, and Gao Z 2010 Development and field pilot of a novel viscoelastic anionic-surfactant (VAS) fracturing fluid SPE Western Regional Meeting
[4] Armstrong K, Card R, Navarrete R, Nelson E, Nimerick K, Samuelson M, and Wasylycia N 1995 Advanced fracturing fluids improve well economics Oilfield review 7(3) 34-51
[5] Jennings Jr A R 1996 Fracturing fluids-then and now Journal of petroleum technology 48(07) 604-610
[6] Samuel M, Card R J, Nelson E B, Brown J E, Vinod P S, Temple H L, Qu Q and Fu D K 1997 Polymer-free fluid for hydraulic fracturing SPE annual technical conference and exhibition
[7] Wang X, Zou H, Chen Y, Zhang F and Peng J 2004 Development of a Novel Alcoholic Acid System for Removal Damage Resulting from Hydraulic Fracturing in the Tight Gas Reservoir SPE International Symposium and Exhibition on Formation Damage Control
[8] Sanchez R H, Agut R G, Coulon D and Sentinelli R 2007 New Methodology of Effective Hydraulic Fracturing in High-Thickness Formation Latin American & Caribbean Petroleum Engineering Conference Society of Petroleum Engineers
[9] Dantas T N C, Santanna V C, Neto A A D, Curbelo F D and Garnica A I 2006 Methodology to break test for surfactant-based fracturing gel Journal of Petroleum Science and Engineering 50(3-4) 293-298
[10] Santanna V C, de Castro Dantas, T N and Neto A A D 2012 The Use of Microemulsion Systems in Oil Industry Microemulsions: An Introduction to Properties and Applications 161-174
[11] Boyer C M, Glenn S A, Claypool B R, Weida S D, Adams J D, Huck D R and Stidham J E 2005 Application of viscoelastic fracturing fluids in Appalachian Basin Reservoirs SPE Eastern Regional Meeting
[12] Willberg D M, Card R J, Britt L K., Samuel M, England K W, Cawiezlel K E, Krus H 1997 Determination of the effect of formation water on fracture fluid cleanup through field testing in the East Texas Cotton Valley SPE Annual Technical Conference and Exhibition
[13] Lee C C, Darby M C, Popp T R 2001, January Effective thru tubing gravel pack methods in Attaka Field SPE Asia Pacific Improved Oil Recovery Conference
[14] Bustos O A, Heiken K R., Stewart M. E, Mueller P M, Lipinski E, Bui T 2007 Case Study: Application of a Viscoelastic Surfactant-Based CO₂ Compatible Fracturing Fluid in the Frontier Formation, Big Horn Basin, Wyoming In Rocky Mountain Oil & Gas Technology Symposium Society of Petroleum Engineers

[15] Fredd C N, Olsen T N, Brenize G, Quintero B W, Bui T, Glenn S, Boney C L 2004 Polymer-free fracturing fluid exhibits improved cleanup for unconventional natural gas well applications SPE Eastern Regional Meeting Society of Petroleum Engineers

[16] Sullivan P F, Gadtryar B R, Morales R H, Holicek R A, Sorrells D C, Lee J and Fischer D D 2006 Optimization of a visco-elastic surfactant (VES) fracturing fluid for application in high-permeability formations SPE International Symposium and Exhibition on Formation Damage Control Society of Petroleum Engineers

[17] Chen Y, Pope T L and Lee J C 2005 Novel CO₂-emulsified viscoelastic surfactant fracturing fluid In SPE European Formation Damage Conference Society of Petroleum Engineers.

[18] Luo X, Wang S, Wang Z, Jing Z and Lv M. 2014 Experimental research on rheological properties and proppant transport performance of GRF–CO₂ fracturing fluid. Journal of Petroleum Science and Engineering, 120, 154-162

[19] Hall R 2005 Novel CO₂-emulsified viscoelastic surfactant fracturing fluid system SPE Annual Technical Conference and Exhibition Society of Petroleum Engineers.

[20] Sun X, 2019 Development and evaluation of a novel seawater-based viscoelastic fracturing fluid system Journal of Petroleum Science and Engineering, 183 p106408

[21] Yan Z 2016 Development, formation mechanism and performance evaluation of a reusable viscoelastic surfactant fracturing fluid Journal of Industrial and Engineering Chemistry, 37 p 115-122