Developing New Recyclable and CO₂ Sensitive Amphiphile for Fracturing Fluid

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Abstract. With rapid development of unconventional shale gas and tight oil, hydraulic fracturing is playing a critical role in oil & gas exploitation and stimulation. Meanwhile, damage to the reservoir fracture and environmental contamination caused by fracturing flowback water has raised serious concerns. In this study, we develop a novel amphiphilic VES fracturing fluid that is not only rock formation friendly and environment benign but also can readily be reused, and with a gelling-breaking process be easily controlled by different gas conditions. We synthesized a CO₂-responsive surfactant C₂₂ZEA which can be used as a thickening agent for hydraulic fracturing fluid. The basic properties of the C₂₂ZEA are studied. Then the different phase behaviour of this CO₂-responsive fracturing fluid was investigated through rheological measurements under ambient and elevated temperature and pressure. The fluid-rock interaction was lastly studied in the core flooding tests. The good CO₂ responsiveness and switchability in viscoelasticity portend the achievable reused of this VES fluid; most interestingly, this fluid exhibits noticeable shear tolerance and CO₂ pressure responsive behaviors which has great potential to realize the reclamation of VES fracturing fluid, and the fracturing fluid exhibits better performance under supercritical CO₂ condition.

1. Introduction

As the conventional oil reserves in the world continue to decline, the immense deposits of tight oil and natural gas attract much attention[1, 2]. Fracturing oil & gas wells is a well-established practice for productivity enhancement in petroleum reservoirs and has been used for more than 60 years all over the world[3]. Because the tight oil and natural gas are stored in ultra-low permeable rock formations, the application of hydraulic fracturing is required in order to economically extract the oil and gas resources from these reservoirs. Fracturing is a stimulation treatments to greatly improve well productivity by creating high conductivity fractures between the area surrounding wellbores and ultra-low permeability reservoirs through high pressure fracturing fluid pump[4]. The design, property and behavior of the fracturing fluid are critical to the success of reservoir fracturing. The main functions of these fluids are to create fractures and transport proppants into the fractures, and which all based on their excellent viscoelastic properties[5]. Meanwhile, the minimal influence of the pore structures and gas & oil seepage after gel-breaking is another consideration.

Nowadays, water-based fracturing fluid is still the dominant position in the application of fracturing. Guar gum and its derivatives are widely used and still play an important role in today’s hydraulic fracturing[6, 7]. Whereas, insoluble residues generated from the guar gel broken always causes undesirable damage to the reservoir rock and a growing concern over the contamination of
hydraulic fracturing flowback water[8, 9]. The environmental and safety issues encourage the development of more environmentally friendly hydraulic fracturing fluids. Studies to enhance properties of hydraulic fracturing fluids have found that viscoelastic surfactant (VES) solution can improve the productivity of gas and oil efficiently extracted after fracturing. Based on the dynamic reversible three-dimensional network structure, the VES exhibits excellent viscoelastic properties. Compared with conventional polymer fracturing fluid, VES fracturing fluid has many advantages, such as few components, easy preparation, good proppant transport capacity, low treatment friction, no residue, low damage to cracks and formations, and no additional breaker. The VES fracturing fluid requires no chemical breakers, yet cleans up better than crosslinked polymer fluids, leading to a lower skin and greater well productivity[4, 10].

Nevertheless, high cost, relatively low temperature resistance and potential environmental risk have been reported as the main shortcomings as the VES fracturing fluid[11]. One strategy for overcoming shortcomings is to reuse VES fracturing fluid with some replenishes. Currently, CO₂ responsive VES solution presents superior advantages, because environmentally benign and abundant CO₂ is a truly mild and green trigger in practical applications[12]. Compared to other triggers such as temperature, light and electric field, CO₂ has a lot of advantages that can be applied to hydraulic fracturing fluid[13, 14], for example, it is inexpensive, nonhazardous, and easily removed. Meanwhile, the physical association and dynamic reversible entanglement of wormlike micelles present good viscoelastic properties of proppant transport. The good CO₂ responsiveness and switchability of system viscoelasticity portend the achievable reused of this sequence. By offering far more flexibility than traditional surfactants, CO₂ switchable surfactants make it possible for the one molecular to full-fill two roles. Since Jessop report reversible nonpolar-to-polar solvent upon exposure to an atmosphere of CO₂, numerous researches on the performance and application of CO₂ triggered systems have sprung up[15]. But the temperature resistance of VES system is always a great problem[16, 17], and few researches take focus on the influence of high temperature on the performance of CO₂ triggered systems. Therefore, many studies are needed to resolve those shortcomings involved in viscoelastic system with CO₂ response in order to reinforce its properties[4, 15, 18]. To our best knowledge, no existing VES fracturing fluid based on CO₂ triggered switchable systems are reported. So, to introduce CO₂ triggered surfactants into fracturing fluid will provide a new possibility to reuse of hydraulic fracturing fluid.

As mentioned above, the main theme of this study is to introduce a CO₂ responsive VES fracturing fluid which can be recycled. The rheological properties, temperature resistance and flowback fluid reclamation were characterized. Firstly, we synthesized C_{22}ZEA as a thickening agent for hydraulic fracturing fluid, sodium salicylate (NaSal) was added to system as a counter-ion. Then, its viscoelastic behaviours depend on temperature and CO₂ pressure were investigated by rheological measurements. Thirdly, fracturing fluid performance and recycle property were studied. We expect this study can have potential applications not only in enhanced oil recovery, but more areas such as microfluidics and underground water pollutions.

2. Materials and experiments

2.1. Materials
Potassium chloride, sodium chloride, magnesium chloride, calcium chloride, sodium salicylate (NaSal, NaCa_{6}H_{4}CO_{2}, 99.5%), erucic acid, N,N-dimethyl-1,3-propanediamine (DMPDA), NaF, and Al₂O₃ were purchased from Aladdin Reagent CO, Ltd. (Shanghai, China) and used as received. Carbon dioxide (99.9%) and nitrogen (99%) were purchased from Oxarc Inc. USA.

C_{22}ZEA with purity greater than 99.0% (HPLC) was synthesized following to a previous procedure[19] with modifications. Erucic acid was reacted with DMPDA without solvent, and NaF was used as a catalyst. The reaction mixture was refluxed at 155-160°C under a nitrogen atmosphere for 12 h, during which by-product H₂O was absorbed continuously by Al₂O₃ placed in a solvent still-head distillation apparatus. When the reaction was terminated, the raw EA product was washed with a
solvent of acetone and water mixture (at volume ratio of 2:1) to remove the catalyst and residuals. Washing was continued until no DMPDA was found by the thin-layer chromatography. The purified EA was then dried under a vacuum to obtain the final product (>99%). The synthesis route is shown in Scheme 1.

Scheme 1. Synthetic route of C_{22}ZEA molecule

2.2. Surface tension measurement

Surface tension measurements were carried out on a Model JYW-200B surface tensiometer (Chengde Dahua Instrument Co. Ltd.) using the ring method. Temperature was controlled by a oven. The surface tension was determined by a single-measurement method and all measurement were repeated at least three times.

2.3. Rheological measurement

Steady and dynamic rheological measurements were performed by a rotational rheometer (MCR101, Anton Paar GmbH, Graz, Austria) using concentric cylinder geometry CC27 (SN21878) and stress-controlled mode, with a temperature-controlling Peltier unit and a sample cover to minimize evaporation. The temperature was controlled by circulation thermostat when the measure temperature is higher. Pressure cell geometry CC25 (STD) with temperature and pressure controller was performed to measure the fluid at different CO\(_2\) pressures. All the sample before measure will kept in the desire temperature for more than 10 minutes’ equilibrium time. All rheological measurements were carried out under the condition of a linear range of strains. All relaxation modes of the systems with certain temperature were determined in the same way, and a master curve could be obtained by means of time-temperature superposition.

3. Results and Discussions

3.1. Surface tension

Surface tension measurements were introduced to character the different aggregation behaviour and cmc of C\(_{22}\)ZEA before and after bubbling of CO\(_2\) in aqueous solutions at 25 \(^{\circ}\)C. The surface tensions as a function of surfactant concentrations are shown in Figure 1. The surface tension decreases sharply with the increasing C\(_{22}\)ZEA concentrations in low concentration region, which indicate that good adsorption can be formed at the water/air interface before and after bubbling CO\(_2\). The surface tension of the systems tend to be a constant when the concentration of surfactants increases, the breakpoint of these two regions is assigned to the cmc. As the concentration of system is greater than cmc, the formation of the micelle in the system is predicted. Two systems can form micelles at very low concentrations, C\(_{22}\)ZEA solution without CO\(_2\) has a lower cmc than C\(_{22}\)ZEA solution in present of CO\(_2\) (C\(_{22}\)ZEA-H\(^+\)), this may be due to the greater electrostatic repulsion between its headgroups as the protonated structure formed after bubbling of CO\(_2\). And the system after bubbling CO\(_2\) has lower surface tension, which may be due to the formation of interfacial activity of protonated proton from structure to make it stronger.

In order to further identify the difference of C\(_{22}\)ZEA solution with and without CO\(_2\) in the ability to reduce surface tension of solutions, the effectiveness of the surface tension reduction (\(\Pi_{cmc}\)) is calculated by the equation(1); the surface excess concentration (\(\Gamma_{max}\)) of C\(_{22}\)ZEA molecule at water/air interface was determined through the Gibbs equation(2); the minimum area (\(A_{min}\)) occupied per surfactant at the interface can be obtained from equation(3)

\[
\Pi_{cmc} = \gamma_0 - \gamma_{cmc} \tag{1}
\]

\[
\Gamma_{max} = -\frac{1}{2.303nRT} \left(\frac{\partial\gamma}{\partial \log C}\right)_T \tag{2}
\]

\[
A_{min} \tag{3}
\]
A_{\text{min}} = \frac{1}{N_A} \times 10^{23} \text{ (3)}

Where, γ₀ is the surface tension of the deionized water and γ_{cmc} is the surface tension of C22ZEA solution when its concentration is above the cmc; gas constant (R=8.314 J·mol⁻¹·K⁻¹); T is the absolute temperature in Kelvin; factor n is the number of solute species whose concentration at the interface changes with the change of surfactant concentration C, here n is taken as 2; Avogadro’s number Nₐ=6.023×10^{23} mol.

Figure 1. Surface tension isotherms at 25 ºC as a function of concentration of C_{22}ZEA and C_{22}ZEA-H⁺.

Specific thermodynamic parameters is shown in Table 1. The difference between surface tension reduction and surface excess concentration of these two system is significant, this may because the protonated headgroup in present of CO₂.

| Molecule       | cmc(mM) | γ_{cmc} (mN·m⁻¹) | Π_{cmc} | Γ_{max} (umol·m⁻²) | A_{min} (nm²) |
|-----------------|---------|------------------|---------|-------------------|---------------|
| C_{22}ZEA-H⁺    | 0.060   | 29.0             | 43.0    | 4.27              | 0.39          |
| C_{22}ZEA       | 0.035   | 32.5             | 39.5    | 3.88              | 0.43          |

3.2. Rheological behavior
To study the viscoelastic and CO₂-responsive behavior of the C_{22}ZEA aqueous solution at ambient temperature and pressure, both steady-state and frequency sweep rheological measurements were carried out under ambient pressure and 25ºC. The plateau value of steady viscosity at low shear rate was used to extrapolate the zero-shear viscosity in steady-shear measurements.
Phillip[20] et al. reported that proppant was transported more efficiently in the region of elastic transport typical of VES fracturing fluids than in the region of purely viscous transport. Storage modulus G' describes the elastic properties of the solution, while the loss modulus G'' is proportional to the viscous resistance. Frequency measurements were applied to further explore the viscoelastic behaviors of these solutions. The variation of G' and G'' as a function of frequency at ambient temperature and pressure are shown in Figure 2a, the G' and G'' increased with the increasing C\textsubscript{22}ZEA concentration. The dynamic rheological results show that the G' was dominating the G'' over the high frequencies range of the measurement when concentration is higher than 3 wt%, this is a typical elastic hydrogel, i.e. a solid like gel with tolerance to external force. Meanwhile, the plateau modulus G\textsubscript{0} is related to the number density of aggregates and consequently show the mesh size of the network. The difference of G\textsubscript{0} corresponds to the different degree of wormlike micelles entanglement, therefore can be regarded as an evidence of one dimensional micellar growth. The results show that the C\textsubscript{22}ZEA concentration is related to the length of wormlike micelle, leading to an increase in viscoelasticity. This VES fluid based on C\textsubscript{22}ZEA can form a transient network structure because the entanglement of the polymer like wormlike micelle, strongly enforced by non-covalent interactions.

Switchability is the basis property for the system to be recycled. This VES fluid of C\textsubscript{22}ZEA was sensitively responding to the interaction with CO\textsubscript{2}, the shear viscosity could be turned on and off by adding and removal CO\textsubscript{2} from the system. As shown in figure 2b, the initial zero-shear viscosity of C\textsubscript{22}ZEA solution before bubbling CO\textsubscript{2} was 2.6 mPa·s; after bubbling CO\textsubscript{2} through the fluid, the zero-shear viscosity increased to 60000 mPa·s, which was more than 4 orders of magnitude increase. When bubbling N\textsubscript{2}, the zero-shear viscosity returned to its initial value. Such prototype on-and-off switching of high viscosity could be repeated several times with little changes in the viscosity behavior in each cycle.

### 3.3. Proppant suspension capacity

Proppant suspension capacity is a basic and important property of a fracturing fluid, which affects the quality of fracturing construction. Figure 3 illustrates the effect of concentration on the proppant settling velocity at ambient temperature and pressure. It was obvious that the 4.5 wt% VES fracturing fluid showed stable proppant support properties where on proppant precipitation was observed over 2 hours at 25°C. When the concentration was decreased to 1.5 wt%, the proppant settling velocity was accelerated and the particles settled completely in about 120 minutes. The observed good proppant suspension stability was attributed to the excellent viscoelastic behavior of the VES fluid, whereas high temperature resulted in rapid gel-breaking and quick settling of particles. Decrease of
viscoelasticity and the destruction of 3-dimensional gel structure lead to the inability of the fluid in carrying proppant at high concentration.

![Figure 3. The static proppant suspension experiment of C_{22}ZEA fracturing fluid at different concentrations at ambient temperature.](image)

3.4. Core damage mitigation
Fracturing fluid can leak into the reservoir fracture and increase the irreducible water saturation. Fracturing broken fluid always leaks into the reservoir and adsorbs to the fracture surfaces, which could cause the secondary damage to the formation and reduce oil and gas production efficiency.

The core damage test results for VES fracturing fluids with 1.5 wt% and 3 wt% C_{22}ZEA are shown in Table 2. The permeability damage values were no greater than 10.6%. When the initial permeability was similar, the permeability damage of 1.5% VES broken fluids was slightly smaller than that of 3% VES, and permeability damage increases when the core permeability was smaller. In comparison, the traditional guar gum fracturing fluid cased much severe core permeability damage, with about 55%. The insoluble residues of guar gum fracturing fluid block the pore throats in formation, while the VES fracturing fluid can be mostly converted to spherical micelles with gel breaking and be recovered. Thus, the permeability damage caused by this VES fracturing fluid is much lower compared to that caused by the traditional guar gum fracturing fluid.

Table 2. Petrophysical properties of the cores and the damage of core sample permeability by different concentrations.

| Core No | Concentration of EA | Length (mm) | Diameter (mm) | Porosity (%) | Initial permeability ($10^{-3} \mu m^2$) | Final permeability ($10^{-3} \mu m^2$) | $\eta_d$ (%) |
|---------|---------------------|-------------|---------------|--------------|----------------------------------------|---------------------------------------|------------|
| 1       | 3%                  | 70.39       | 25.21         | 13.48        | 189.3                                  | 169.2                                 | 10.6       |
| 2       | 3%                  | 71.25       | 25.25         | 17.01        | 526.3                                  | 490.2                                 | 6.8        |
| 3       | 1.5%                | 69.95       | 25.13         | 22.60        | 945.2                                  | 928.8                                 | 1.7        |

4. Conclusions
In this research, a CO$_2$-responsive surfactant C$_{22}$ZEA was synthesized and used as the thickening agent in VES fluid to form a novel fracturing fluid that was not only rock formation friendly and environment benign but also reusable. This CO$_2$-responsive VES fracturing fluids exhibited good viscoelastic which is critical for proppant transport. The fluids were easily switchable between high and low by manipulating the presence of CO$_2$. Rapid viscosity increase of the VES fluid in responding to the presence of CO$_2$ can endow a potentially application of this fluid as a leakage sealant at the cap rock formations of geological carbon sequestration reservoirs. The low core damage indicated that this
VES fracturing fluid was formation and fracture friendly. A distinct advantage of this fracturing fluid over others is the use of environment benign stimuli CO$_2$ as the trigger for the gel-solution switching.

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