



Development of CO₂-Sensitive Viscoelastic Fracturing Fluid for Low Permeability Reservoirs: A Review

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Abstract: There are economic and technical challenges to overcome when increasing resource recovery from low permeability reservoirs. For such reservoirs, the hydraulic fracturing plan with the development of clean and less expensive fracturing fluid plays a vital aspect in meeting the energy supply chain. Numerous recent published studies have indicated that research on worm-like micelles (WLMs) based on viscoelastic surfactant (VES) fluid has progressed substantially. This study looks at the development of CO₂-sensitive viscoelastic fracturing fluid (CO₂-SVFF), its applications, benefits, limitations, and drawbacks of conventional fracturing fluids. The switchable viscoelasticity of CO₂-SVFF system signifies how reusing of this fluid is attained. Compared to conventional surfactants, the CO₂-SVFF system can be switched to high viscosity (to fracture formation and transporting proppants) and low viscosity (easy removal after causing fracture). The effect of pH, conductivity, temperature, and rheological behaviors of CO2-SVFFs are also highlighted. Further, the aid of Gemini surfactants and nanoparticles (NPs) with low concentrations in CO2-SVFF can improve viscoelasticity and extended stability to withstand high shear rates and temperatures during the fracturing process. These studies provide insight into future knowledge that might lead to a more environmentally friendly and successful CO₂-SVFFs in low-permeability reservoirs. Despite the increased application of CO₂-SVFFs, there are still several challenges (i.e., formation with high-temperature range, pressure, and salinity).

Keywords: low permeability reservoirs; fracturing fluid; worm-like micelles; rheology; CO₂-sensitive viscoelastic surfactant

1. Introduction

Hydraulic fracturing is an efficient stimulation method for generating highly conductive conduits between wellbores and low permeability reservoirs [1,2]. Pressurized fluid containing proppants is injected into the low permeability reservoirs to keep the fracture open [3,4]. This method includes constructing and enlarging conductive conduits through which the hydrocarbon can flow easily. The fracture network formed improves the reservoir rock's hydraulic conductivity while increasing the surface area available for hydrocarbon production [5,6]. Fracturing fluids are used to create artificial fractures in reservoirs and transport proppant particles into the cracks to improve formation conductivity [7–9]. Pad or prepad fluids are initially pumped into the formation to create the fracture geometry. After the fracture geometry has been generated, a more fluid-carrying proppant is transported into the fractures. The proppant prevents fracture closure by providing a conductive conduit for hydrocarbons to flow back into the wellbore [10–12]. Proppant transport is



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). influenced by the fracturing fluid's rheology, proppant properties, and fracture geometry. The fracturing fluid must be economical, compatible with the formation, residue-free, have a lot of fracturing experience and withstand high temperatures and shear rate [13].

In the past, oil-based fracturing fluids were utilized in hydraulic fracturing. Since oil-based fracturing fluids have been linked to environmental and safety problems, the industry has been developing more environmentally acceptable water-based fracturing fluids [14]. Several polymers were utilized to improve the viscosity of the fracturing fluid due to low water viscosity. Borate, titanium, and zirconium cross-linkers increase polymers' gel strength and viscosity [15-17]. On the other hand, the polymer fracturing fluid leaves insoluble residues that reduce the formation's permeability [18–20]. Limited sand carrying capacity is the other drawback of this fracturing fluid [21]. Chemical EOR [22], gravel packing [23], drilling [24,25], and hydraulic fracturing [7] can all benefit from the use of viscoelastic fluids that are polymer-free. Shell developed viscoelastic surfactants (VESs) to solve the polymer fluid problems in hydraulic fracturing [26,27]. VES fracturing fluids provide several advantages over polymer fracturing fluids [28,29]. The advantages including the absence of insoluble residues, low-pressure friction, gel breaking capacity, ease of preparation, good proppants carrying capacity, and minimal formation damage [30,31]. At high shear rates and temperatures, most VES fracturing fluids, on the other hand, are less durable [31].

This review study is divided into five sections. Surfactants with Viscoelastic Properties, CO₂-SVFFs, Application of CO₂-SVFFs, Properties of CO₂-SVFFs, and their benefits and limits are discussed.

1.1. Surfactants with Viscoelastic Properties

Smaller than guars, viscoelastic surfactants (VESs) have less than a thousand molecular weights. VES-based fluids are polymer-free fluids widely used in hydraulic fracturing [13,32]. Under certain conditions, VESs can self-assemble into colloidal forms recognized as worm-like micelles due to repelling and attractive interactions between the surfactants and the solvents. Worm-like micelles with contour lengths varying from a few nanometers to several micrometers [33,34]. The worm-like micelles tangle into a transient network beyond a threshold concentration c*, identical to a solution of flexible polymers with exceptional viscoelastic properties [35,36]. However, in contrast with polymers, it breaks and recombines during the dynamic process.

The hydrophobic tails of surfactant molecules orient themselves toward the inner of the micelles and away from the polar medium (water), resulting in the surfactant molecule's aggregation [37]. Worm-like micelles can provide fracturing fluid with no residues, high conductive stimulation, and high-quality viscoelastic proppant transport characteristics [19,38]. Various self-assembly theories govern micellar assemblages and VES solutions with appropriate interactions and additives under multiple circumstances [39–41]. Critical packing parameters can identify the micelle arrangement in a solution phase. $P = v/a_0 l$, where v is the volume of the surfactant's hydrophobic tail, l is the length of the tail, and a_0 is the surfactant head group's optimal surface [42]. Different micelle configurations in the bulk solution as shown in Figure 1.

The aggregate geometry is stronger when the high packing value [43,44]. The chemical composition of a certain surfactant is often used to develop VES fluids, for instance, anionic, [45,46], cationic [20,47], nonionic [48,49], Zwitterionic/amphoteric [50,51] or a combination of surfactants; cationic/anionic [31,52], nonionic/anionic [53] and Zwitterionic/anionic [54,55]. The sandstone reservoir is better wet by anionic surfactants than cationic surfactants and is less expensive and easier to biodegrade. On the other hand, anionic surfactants exhibit temperature instability. Zwitterionic surfactants have the combined presence of expensive but thermal stability anionic and cationic centers in their heads than other surfactants [44,54]. Zwitterionic surfactants use two different surfactants to increase VES fluid performance [55,56]. Effect of various micelles on surfactant activity and surfactant rheological behavior based on different parameters, for example, surfactant concentration [57], concentration and type of salt [58–60], alkali [60], acid [61], CO₂ [32,62], pH [63,64], temperature [60,65], occurrence of redox reactions [66,67], and light irradiation [68,69]. Some additives may even be required to support surfactants assembled into distinct molecular structures to improve viscoelasticity spontaneously [70,71]. Adjusting the appropriate additive-VES solution level is required for efficient viscoelastic behavior (Figure 1). The morphology of worm-like micelles (WLMs) is influenced by different degrees of ionic strength by salt concentration and types.



Figure 1. The effect of additional counter ions on the behavior of the VES phase [42].

The degree of contra-ion binding is determined by the hydrophobicity and micellization of the counterion. Electrostatic screening for the repulsion between the surfactant head groups occurs by oppositely charged counterion ions due to organic or inorganic salts mixed with various surfactants. Halide ions from organic salts such as Cl⁻ or Br⁻ are considered to be adsorption to the micelle surface based on weak to relatively weak interactions with the surfactant cations. Whereas inorganic salts such as sodium salicylate (NaSal) are tightly bound to the surface head groups, micelle form transition improves when salt concentration decreases [72,73]. The micelle disrupts under certain shear forces, yet it assembles its initial form again after applying shear stress to eliminate [74], in contrast to the polymer degradation process, which can reversibly deteriorate after shear stress [75,76]. Hydrocarbons or formation water can break the structure of the VES fluid, reduce its viscosity, and thus, no chemical or chemical breaker requirement [77,78]. VESbased fracturing fluids are more stable over a certain salt concentration, and the gel can be broken easily by diluting with the formation fluids. Hydrophobic substances such as oil or gas are dissolved in the hydrocarbon core of the micelle, and the structure stretches and fractures into smaller spherical micelles [30]. The VES fluid does not break completely in dry gas or low oil saturation reservoirs; hence an internal breaker is necessary. An internal breaker distracts the VES micellular structure and reduces viscosity [70,79]. In addition, low molecular weight alcohols or oxidizing breakers may disintegrate WLMs into non-viscous spherical micelle or destroy the structure of surfactant molecules [30]. Numerous researchers used various improvements in the study of the quality of VES fracturing fluid (VFF) [4,80]. In addition, experimentation and field applications are less documented [79,81]. The WLMs in micellar fluids are remarkably similar to polymers; hence they are constantly dispersed and recombined at equilibrium [82]. However, the high cost, environmental problems, high temperatures, and high salt concentration are

some of the limitations of mostly conventional VES fluids [83,84]. Viscoelastic surfactant system is always resistant to poor temperature. At high temperatures, the molecular thermal motion rates increase, molecules' strength decreases, and the CMC of surfactants rises geometrically [85]. The primary disadvantages of VES fracturing fluids, on the other hand, are their high costs, limited temperature resistance, and potential environmental concerns [32,86]. These issues must be overcome by re-usable viscoelastic surfactant (rVES) fluid, VES/CO₂ fluid, VES/NP fluid, and Gemini-VES fluid [87–89]. In Gemini surfactants, a spacer group connects 2 or 3 hydrophilic head and hydrophobic tail groups [90].

Several review studies on various viscoelastic surfactants used for hydraulic fracturing procedures have been published. The study of smart worm-like micelles (SWLMs), which can reversibly change the rheological behavior from low viscosity to higher viscoelasticity, has recently gotten much attention [91–94]. Temperature, pH, light, and redox potential have all been used previously to "turn" micellar assemblies ON and OFF. Each has its disadvantages, such as spatial restriction, excessive usage of energy, or contamination, limiting the process's reversibility [88]. Conventional triggers have drawbacks; for instance, surfactant space on thermos-responsive triggers would be restricted [95].In the field of fracturing fluids, VES is a study issue; nevertheless, fracturing fluid flow-back can create significant environmental concerns [96].

1.2. CO₂-Sensitive Viscoelastic Surfactants

 CO_2 –SVFF solution offers better benefits because environmentally friendly and plentiful CO_2 may be used as a green trigger in practical applications. CO_2 has many other advantages that may be used in hydraulic fracturing fluid, including being inexpensive, non-hazardous, energy-efficient, and easy to remove from the system [31]. The current study will explain how CO_2 induced in viscoelastic surfactants fluids improves its properties compared to previous research.

Mathew Samuel et al. [97] worked on the development in fracturing fluids, introducing a polymer-free VES fluid that is CO₂-compatible. R. Hall et al. [37] developed a novel multisurfactant clean fracturing fluid system to provide a strong surfactant-based fracturing fluid with the addition of CO₂. The field test findings of his study showed that the fluid system is CO₂ compatible and exhibits all of the attributes generally associated with VES systems. Adjusting the appropriate additive-VES solution concentration is required to properly manage the viscoelastic behavior as shown in Figure 2. According to multiple research publications on the subject, CO₂ is useful in extracting oil from low permeability oil reservoirs because it increases oil swelling, decreases viscosity, and vaporizes components of crude oil as it is carried through porous rock [98].



Figure 2. Sketch diagram displaying the preparation process of CO₂-SVFF.

CO₂-SVFFs have attracted many researchers' attention in the last few years [99]. CO₂ can improve the viscoelasticity and aggregate structure of VES fluids. CO₂-SVFFs containing WLMs are extraordinarily viscous and elastic because of their physical association and entangled structures [41]. In four different forms, CO₂-responsive functional groups are found in conventional CO₂-responsive surfactants (tertiary amine, amidine, guanidine, and imidazoline) [100]. Compared to the others, tertiary amines are a traditional chemical product as a conventional functional group. It responds well to CO₂ and has simple production methods. As illustrated in Figure 3 below, there have been several CO₂-responsive compounds [101].



Figure 3. CO₂-responsive functional groups that are commonly used [101].

In a fixed proportion, an anionic surfactant and its counterion are added to generate spherical VESs. After CO₂ bubbling and protonation, spherical micelles convert into WLMs. The CO₂-induced VES showed a reverse transformation after the pH was changed. This fluid can be reused due to its CO_2 responsiveness and switchable viscoelasticity. CO_2 -responsive switchable surfactants can perform two functions at once, fracturing and proppant transport and recovery following fracturing, by switching between high and low viscosity [32]. Inspired by the pseudo-Gemini idea work, Zhao et al. [102] constructed a CO2-sensitive anionic SWLMs system using sodium oleate (NaOA) and the small chemical counter ion 2,6,10-trimethyl-2,6,10-triazaundecane (TMTAD). The 3NaOA-TMTAD solution was initially transparent, having low viscosity and spherical micelles (the primary morphology), as shown in Figure 4. This system exhibits significant viscosity, transparency, and aggregates of mostly wormlike micelles after a duration of CO₂ introduction. TM-TAD and NaOA were mixed in a 1:3 ratio based on electrostatic interactions to generate a pseudo-Gemini surfactant. The combined solution looks turbid and has low viscosity soon after the excess CO_2 is introduced, possibly due to the lower solubility of the NaOA molecules. Sodium hydroxide can be introduced to the system to change the agglomeration

forms of the solution. In the same kind of work, Shaikh et al. [103] presented a Novel CO_2 -induced clean fracturing fluid (SDS-TMTAD- CO_2) created using simulated formation water (23,003 mg L⁻¹). Rheological investigations revealed that the apparent viscosity of the fracturing fluid system increases to some degree under high salt conditions and has sufficient self-healing properties against high shear tolerance.



Figure 4. The system's self-assembly technique, triggered by CO₂, is schematically illustrated [102].



Figure 5. The figure depicts the Pseudogemini Surfactant Micellar System's Switching Mechanism [88].

In another research by Zhang et al. [104], the viscoelastic wormlike micelles generated by natural sodium erucate ($C_{22}H_{41}NaO_2$) after bubbling CO₂ were studied. In addition, the rheological behaviors of micellar solutions compared to another carbon dioxide–responsive wormlike micelles were investigated. It becomes turbidity when 100 mM erucic acid aqueous solution is combined with bubbling carbon dioxide at 60 °C to saturation (pH = 6.63). After bubbling nitrogen at 85 °C to replace carbon dioxide, the pH raised to 9.22 (9.72 at 100 °C), at which point the solution becomes less viscous and turbidity decreases. After

adding NaOH, a transparent viscoelastic solution was obtained after altering the pH of the solution to 10.63.

A study by Zhang et al. [100] found that the viscoelastic aqueous phase contains only the surfactant *N*-erucamidopropyl-*N*, *N*-dimethylamine (UC22AMPM, Figure 6), and CO₂, with no hydrotropes, which are generally required in conventional WLMs to facilitate micelle development via screening strong surfactant binding or electrostatic repulsions between charged surfactant head groups.



Figure 6. The mechanism that governs CO₂-air switchable wormlike micelles "Reproduced with permission from Ref. [100]; 2022, Royal Society of Chemistry".

2. Application of CO₂-Sensitive VES as Fracturing Fluid

There are limitations in slick-water volume fracturing and gas injection to add energy for drainage and displacement [105]. CO₂ fracturing as waterless technology can increase reservoir pressure after easy flow back, reduce the solid residue and have low damage characteristics [106]. CO₂ diffuses into the matrix, swells the oil, and pushes it into the fractures [37]. CO₂ provides many advantages, including reducing formation damage by reducing solid residue and improving production by boosting reservoir pressure following an easy flow back [107].

 CO_2 -SVFFs with no formation damage is very efficient in low permeability reservoirs. CO_2 -SVFFs can generate fractures in the rock, substantially improving permeability near the wellbore, resulting in a high production rate with low-pressure decline [103]. CO_2 dissolves into oil, reducing interfacial tension and oil viscosity while also improving the mobility ratio. The CO_2 -SVFFs assist in reducing the quantity of water utilized in traditional VES fracturing fluids. CO_2 is also non-toxic, non-explosive, and relatively inexpensive [108]. CO_2 -SVFFs have the potential to improve oil/gas recovery from low-permeability reservoirs significantly.

3. Properties CO₂-Sensitive Viscoelastic Surfactants

The efficiency of CO₂-induced clean fracturing fluid is influenced by pH, conductivity, viscosity, shear rate, salt concentration, pressure, temperature, and rheological behavior.

3.1. Effect of pH

As the pH of a solution approach complete ionization, the viscosity of the solution decreases [35,88,109]. The pH level of the solution dropped as CO₂ was bubbled into it, and the viscoelastic characteristics altered as the chemical configurations changed [95].

As shown in Figure 7, 150 mM sodium oleate (NaOA) and 50 mM 2,6,10-trimethyl-2,6,10-triazaundecane (TMTAD), a small organic counterion, were introduced in water [102]. At an exact stoichiometric ratio of 3:1, a clear water-like solution with a pH of 12.17 was produced. After CO_2 bubbling, a clear, homogeneous, and very dense solution formed with a pH of about 9.17.



Figure 7. At ambient temperature, zero-shear viscosity of 150 mM NaOA and 50 mM TMTAD in aqueous solution with bubbling CO₂ (reduction in pH) [102].

In another study, Zhang et al. [110] developed CO_2 -induced anionic wormlike micellar fluid by combining triethylamine (TEA) with the natural anionic surfactant sodium erucate (NaOEr) at a molar ratio of 3:10 (CNaOEr: CTEA). While CO_2 is bubbled into the solution, the pH drops from 12.3 to 10.0. TEA is protonated into a quaternary ammonium salt, promoting micelle formation by reducing electrostatic repulsion between anionic head groups in NaOEr molecules. After CO_2 is removed, the quaternized TEA deprotonates back into a non-ionic tertiary amine, resulting in wormlike micelles. As a result, electrostatic repulsion strengthens, converting the viscoelastic fluid to its original low viscosity spherical micellar solution.

3.2. Effect of Conductivity

Monitoring the conductivity of a solution while CO_2 and then any inert gas bubbled through the solution over different cycles, as shown in Figure 8, can demonstrate the process' reversibility and repeatability [111].

Liu et al. [95] utilized *N*-butyldiethanolamine sodium oleate (BDEA-NaOA) and *N*,*N*-diethylbutylamine–sodium oleate (DEBA-NaOA) to make two types of CO₂-responsive wormlike micelles. The BDEA-NaOA and DEBA-NaOA combination systems generated wormlike micelles after CO₂ was bubbled into the solution. As a result, the conductivity and pH level were used to investigate the impact of CO₂ on the solutions. After CO₂ bubbling into the BDEA-NaOA solution, the conductivity promptly increased and peaked after 20 min, as the tertiary amine protonated to quaternary ammonium salt. At the same time, with the blubbering of CO₂, the pH value essentially declined.



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Figure 8. The conductivity of a Dimethyl sulfoxide (DMSO) solution as a time-dependent throughout 3 phases of CO₂ treatment followed by argon at 23 °C [111].

3.3. Effect of Viscosity

The relationship between CO_2 and VES fluid viscosity is quite sensitive. VES may turn on and off the high viscosity by adding and removing CO_2 from the system. The low-andhigh zero-shear viscosity cycle was implemented using two separate ways (bubbling gas and heating) [32], as illustrated in Figure 9. The zero-shear viscosity of a 3% EA solution without CO_2 bubbling was 0.0026 Pa·s. Still, after bubbling of CO_2 , the viscosity jumped to 6 Pa·s.The protonation of VES with CO_2 improves the viscosity of CO_2 -SVFF by increasing the packing parameters by 1/3-1/2. Deprotonation proceeded after N₂ bubbling, lowering the viscosity to its original levels.

In other studies, Zhang et al. [112] reported a 2.0 wt% octadecyl dipropylene triamine (ODPTA) dispersion is milky and low-viscosity at room temperature (Figure 10A), but instantly transforms to a clear viscoelastic "gel" following two minutes of CO₂ bubbling ("ODPTA-CO₂"), which is suitable for trapping bubbles for longer durations (Figure 10B). The "gel" regains its original appearance after replacing CO₂ with N₂ at 75 °C for approximately 45 min (Figure 10C). Instead of using HCl to bring the pH down to 6.0, a transparent, water-like fluid (Figure 10D) is produced, with no viscoelastic properties.

Su et al. [113], found that aqueous solutions containing both 2-(dimethylamino) ethanol (DMAE) and the surfactant sodium octadecyl sulfate (C_{18} SNa) are CO₂-responsive (Figure 11a); CO₂ tends to cause protonation of DMAE in water, and an enhance in zero-shear viscosity at 60° C (Figure 11b), indicating micelle elongation. The viscosity of VES fluid measurements to verify that the switch is reversible after bubbled N₂ by removing the CO₂ (Figure 11c). After 50 min, the viscosity reached the same level as distilled water.

3.4. Effect of Shear Rate

Resistant to shear is one of the significant parameters of VES fracturing fluids. Its importance arises when fluid with high speed is injected into the formation [114]. The stability of the VES system at high shear is necessary for hydraulic fracturing processes [4]. At high shearing force, the strength of VES fluid should not be weakened. To efficiently withstand shearing force, the pad fluid of the VES fracturing system should regain the imposed high strength before reaching the formation [46]. At high shearing force, the viscoelastic properties of VES fracturing should have the quick ability to recover [20]. A

CO₂-SVFF based on the long-tailed surfactant Erucic acid 3-(*N*,*N*-dimethylamino) (EADP) was investigated in a study using various ratios of sodium salicylate (NaSal) and maleic acid (MA) [115]. NaSal and "pseudo" Gemini (MA) systems have different types of aggregation of morphologies, such as spherical micelles, worm's preferences, and vesicles.



Figure 9. At atmospheric temperature and pressure (unless when gel-breaking at 80 °C), 3% erucamidopropyl dimethylamine (EA) solution with switchable zero-shear viscosity [32].



Figure 10. 2.0 wt% ODPTA aqueous dispersion: (**A**) the initial dispersion; (**B**) bubbling CO₂ (0.1 MPa); (**C**) switching CO₂ with N₂ (0.1 MPa) at 75 °C; and (**D**) altering the pH with HCl as in (**B**) "Reproduced with permission from Ref. [112]; 2022, Royal Society of Chemistry".



Figure 11. The aqueous solution of C18SNa (200 mM) and DMAE (200 mM) was transitioned from low and high zero-shear viscosity phases by switching CO₂ (1 bar) and N₂ (1 bar) treatments for three series at 60 °C (**a**); The water solution was produced by mixing 100 mL distilled water with C₁₈SNa and manually agitating it at 60 °C for several minutes. It was viscous, with a viscosity of 1.1 mPas. After adding the DMAE, the viscosity was 1.2 mPas. After 15 minutes of sparging CO₂ at 60 °C, the solution formed a gel with a viscosity of 26200 mPa·s. (**b**); the viscosity was restored to its previous value of 1.2 mPa·s after sparging N₂ for 50 minutes at 60 °C (**c**). "Reproduced with permission from Ref. [113]; 2022, Royal Society of Chemistry".

Figure 12 shows the steady shear viscoelastic properties of three EADP aqueous systems due to shear rate. As can be observed, the solutions have a characteristic viscosity independent of the shear rate at low shear rates following CO_2 bubbling. At low shear rates, it behaves Newtonian. The viscosity of the EADP solution exhibits a shear-thinning phenomenon once the shear rate is more significant than 0.1 s^{-1} , which can be interpreted as an indication of wormlike micelles that experience a phase transformation the aligning of elongated micelles at a high shear rate. The viscosities of the EADP solution improved throughout the measuring range after 50 mM NaSal was added, which was not the case with the EADP-only system. At low shear rates, the viscosities of the EADP solution increased by order of magnitude when 50 mM Maleic acid (MA) was introduced. At lower shear rates, the viscosity remains essentially unaltered and is nearly equal to the zero-shear viscosity, resulting in Newtonian behavior. The zero shear viscosities of three components execute the sequence MA > NaSal > EADP when CO_2 is present. The viscosity of the solution is low, regardless of the shear rate before the CO_2 bubbles, resulting in Newtonian fluid behavior.

Shaikh et al. [103] performed different rheological experiments to see how different high shear rates (170 and 510 s⁻¹) affected the apparent viscosity of the created fracturing fluid (SDS-TMTAD-CO₂) at 25 °C. The experiment was subdivided into four 600 s time segments. At a shear rate of 170 s⁻¹, the viscosity rose to 163 mPa·s in the first time segment (0–600 s). While at a shear rate of 510 s⁻¹, the viscosity dropped to 105 mPa·s

during the second period (600–1200 s), indicating acceptable viscous behavior against the high shear rate. During the third segment (1200–1800 s), the shear rate was reduced from 510 to 170 s⁻¹ and remained constant. The viscosity against increased to 168 mPa·s in less than a second after the shear rate was reduced, as shown in Figure 13. The shear rate was raised from 170 to 510 s⁻¹ in the last time segment (1800–2400 s), whereas the viscosity declined significantly and remained constant at 107 mPa·s during the whole interval. According to the phenomena, the fluid recovers great viscosity against high shear rates. The interfacial tension (2.3×10^{-2} mN m⁻¹) has good conditions during the flow-back time, clay swelling, and residual oil saturation, respectively.



Figure 12. Shear viscosities in steady-state for 100 mM EADP aqueous systems with various additives (**a**); For EADP solutions with various additives, storage and loss modulus versus frequency (**b**) [115].

3.5. Effect of Salts

The efficiency of fracturing fluids is frequently affected by high salinity in formation water. The viscosity of erucamidopropyl dimethylamine (EA) was measured at a shear rate of 20 s⁻¹ to investigate the effect of salt concentration on CO_2 -SVFFs [32]. The viscosity of the solution had a minimal impact when the salt quantity was low. When salt concentrations increased, the viscosity of the solution decreased somewhat, indicating that the network structure of VES fluids was slightly disrupted, as shown in Figure 14a. With divalent ions, the viscosity of CO_2 -SVFFs decreases to a lesser extent compare to monovalent ions as in Figure 14b. The primary explanation for this could be that EA will shift from nonionic to

cationic surfactant in CO_2 and water, and salt input might affect the cationic head group by screening the electrostatic connection between the cation charged surfactant head groups via the salt electrolyte; as a result, the system's viscosity is reduced slightly [116]. As a result, this Viscoelastic fluid can tolerate high salinity.



Figure 13. Shear resistance test at 25 °C [103].



Figure 14. Shear viscosity of a 3% EA solution with inorganic salts: (**a**) KCl and NaCl are monovalent salts; (**b**) MgCl₂ and CaCl₂ are divalent salts [32].

3.6. Effect of Temperature and Pressure

The temperature has a more significant impact on surfactant molecular thermodynamics. As the temperature rises, the interactions between the head groups of surfactant molecules at the surface weaken [117]. Figure 15 shows the effect of shear time, shear rates, pressure, and temperature on the viscosity of CO₂-SVFFs. The rheological properties of CO₂-SVFFs are also significantly influenced by pressure. Without CO₂ pressure, a 2% erucamidopropyl dimethylamine (EA) aqueous solution behaves such as a water-like Newtonian fluid. When 800 psi of CO₂ was added to the system, the fluid's viscosity at a shear rate of 20 s⁻¹ increased by 2-fold compared to the CO₂-free system. The different shear rates affected the fluid's viscosity [32]. The VES fracturing fluid's good rheological performance under supercritical CO₂ circumstances shows much potential for fracturing applications.



Figure 15. Viscosity plots to time for various shear rates and CO_2 pressures and temperatures. (a) At 800 pressure and 25 °C, the viscosity of a 2 percent in an aqueous solution of EA with no CO_2 was low but improved dramatically after bubbling CO_2 . (b) The viscosity of 3% EA at various CO_2 pressures and temperatures of 25 °C. (c) The viscosity of a 3% EA aqueous solution at 25 °C and 70 °C under CO_2 pressure of 1200 psi [32].

3.7. Viscoelastic Behavior

The fluid's viscosity and elasticity play an essential role in suspending the proppants particles in VES fluids [13]. Due to an apparent viscoelastic response (i.e., the behavior is elastic (storage modulus G' >loss modulus G'') at high frequencies, the dynamic rheology of VES aqueous solution in the presence of CO₂ results in the formation of wormlike micelles [37]. Researchers attempted to endow CO₂-reversible responsiveness to the CTAB-NaSal worm (TEA) [117]. The CTAB-NaSal worm was fragmented in the absence of CO₂. It displayed a water-like solution with the appropriate TEA concentration before recovering to highly viscoelastic fluid as bubbling CO₂ due to the shift between spherical micelles and WLMs. Figure 16 demonstrates that bubbling CO₂ generates a mainly viscoelastic response at high shear frequencies, with G' exceeding G''.



Figure 16. (**A**) Static rheology and (**B**) dynamic rheology of 50 mM CTAB-NaSal-TEA before and after bubbling CO_2 at 25 °C (with a molar ratio of 1:1:5) [117].

In a study, different experiments were conducted to explore the viscoelastic behavior of solutions of *N*-butyldiethanolamine–sodium oleate (BDEA–NaOA) and *N*,*N*-diethyl butylamine–sodium oleate (DEBA–NaOA) with CO_2 effect [95]. The pH value reached 8.45, the viscosity remained constant with a rising shear rate, and the solution acted such as water. This type of behavior is characteristic of Newtonian fluids. When the pH value is between 8.65 and 8.45, and the shear rate rises, all samples exhibit Newtonian behavior at first, then shear-thinning behavior at a higher shear rate. The shear-thinning behavior of the wormlike micelles was characteristic of wormlike micelles, showing that wormlike micelles linked with each other in the solution.

3.8. Effect of Gel Structure Breaking and Proppant Suspension and Carrying Capacity

The WLMs in the VES fracturing fluid disintegrate into spherical micelles on interaction with the produced hydrocarbons during flow back, leading to a low viscosity fluid that is easier to remove from the pore space propped fracture [86]. The VES fracturing fluid does not require chemical breakers, and gel breaking is performed by adjusting the fluid-CO₂ interaction [32]. For an excellent Flow back process, the breaking fluid viscosity must be according to the standard, i.e., less than 5 mPa·s [103], as shown the Figure 17. The ability of a fracturing fluid to suspend proppants is a fundamental attribute that impacts the quality of fracturing construction. The viscoelastic qualities of the VES fluid are ideal for proppant transport. CO_2 -SVFFs can perform two functions: high viscosity for fracking and proppant transportation and low viscosity for fracking fluid recovery [32].



Figure 17. Viscosity measurement of gel breaking fluid using kerosene, 25 °C [103].

3.9. Filtration and Permeability Damage Evaluation

Filtration assessment is the most crucial parameter and remains one of the most critical qualities for evaluating reservoir fracturing strategies. If fluid leak-off behavior decreases bottom hole pressure and unequal proppant dispersion, the fracturing work will perform poorly. Different studies analyzed the literature's filtration of CO₂-SVFFs, and the results were outstanding compared to conventional fracturing fluids [103]. It has already been mentioned that if the fracturing fluid is not formation friendly, it will cause problems with fracture conductivity and damage the formation by lowering the formation's permeability [86]. Therefore, the fracturing fluid with low formation damage characteristics is essential in the fracturing technique. Different researchers calculated the formation damage of CO₂-SVFFs using the following Equation (1) [32,41,118].

$$\eta_{d} = \frac{k_1 - k_2}{k_1} \times 100 \tag{1}$$

where η_d is the formation damage ratio in percentage, while k_1 and k_2 are the permeability of the core before and after fluid injection, respectively.

4. Advantages and Limitations

 CO_2 -SVFFs are more effective because of their higher retained proppant pack permeability and controllable rheological behavior. When fracturing with CO_2 -SVFF, viscosity plays a major role in providing sufficient fracture width to ensure proppant entrance into the fracture, carrying the proppant from the wellbore to the fracture tip, generating a desired net pressure to control height growth, and providing fluid loss control. The CO_2 -SVFF is based on the WLMs formation, achieving zero residues, and obtaining highly conductive stimulation treatments with no polymer damage. CO_2 -SVFFs reduce the cost of cleaning, which was found in the water and polymer-based fracturing fluid. Abundant CO_2 can potentially be green which can be used at low cost with a minor amount of surfactant and its counter ion additives. The physical association and entanglement of worm-like micelles present excellent viscoelastic properties of proppant transport, which is better than guar-based fluids.

On the other hand, the fluid system is the most widely used imbibition drainage and displacement system for low permeability oil reservoirs. It could effectively change the wettability of formation and reduce the oil-water interfacial tension, which improves oil

recovery. Coupling the benefits of a VES fluid with CO₂, the emulsified system will further enhance cleanup in a depleted reservoir, extend the application to water-sensitive formations, and maintain reservoir gas saturation to prevent potential water blocks. CO₂-sensitive clean fracturing fluid systems exhibit lower friction pressure, superior proppant transport, higher fracture conductivity, and longer effective fracture half-length than conventional systems by eliminating polymer. Both CO₂ and surfactant can improve low permeability oil recovery by diffusion and imbibition drainage displacement, respectively, which is economically and technically viable. CO₂ with surfactants can dramatically improve CO₂ utilization, surfactant cost reduction, and oil recovery. Given the circumstances, the most recent advancement in fracturing fluids is an ecologically benign and non-polluting CO₂-based clear fracturing fluid.

However, the CO₂-SVFFs technique requires high pump energy compared to the CO₂ fracturing method. Since CO₂ is very mobile, this approach has issues with viscous fingering and gravity overriding due to the limited capacity to control CO₂ mobility. When high-pressure CO₂ is required for VESs, there are issues with handling and safety. When the pressure is released, the CO₂ condenses into dry ice plugs.

5. Future Recommendations

Different researchers used various strategies to improve fluid characteristics, and positive results were observed. More research is needed at high temperatures and pressures for CO₂-SVFFs. The academia and industry must work together to produce VES fluids that respond differently to external stimuli to reduce costs while improving CO₂-SVFF performance in extended reservoir conditions. Furthermore, much experimental research of VES fluids for fracturing concentrated on common aspects such as how temperature impacts the CO₂-SVFFs properties. The studies should be broad to different reservoir conditions. At high pH, the viscosity of CO₂ decreases, so better counter ions should be added to tackle this problem. There has been very little research on CO₂-SVFFs with divalent ions. Further research should include the wettability alteration by CO₂-SVFFs.

Conventional viscoelastic surfactant fluids, which are utilized in large quantities, the viscoelasticity property is reduced when exposed to high temperatures. The Gemini CO_2 -sensitive VES can be employed in small amounts for better results. The rheological characteristics of CO_2 -SVFFs for high-temperature reservoirs and VES systems are required by various hydrophobic chains linked by a spacer group. Nanoparticles should be added to CO_2 -SVFFs to further improve their rheological properties. High-temperature reservoirs tri-cationic surfactants with the required amount of organic salt exhibit excellent rheology and accumulation properties. So further research is needed to use tri-cationic surfactants in CO_2 -SVFFs. The hydraulic fracturing technique is of great importance in developing of shale oil and gas recovery. Further studies of CO_2 -SVFFs in unconventional reservoirs, especially shale, are needed. There is a lack of studies of CO_2 -SVFFs with temperature (≥ 120 °C) and shear rate (≥ 500 s⁻¹). So further studies should also be focused on high temperature and shear rate.

6. Conclusions

In contrast with conventional surfactants, CO_2 -SVFFs are switchable between high viscosity for fracture and proppant transport and low viscosity for easy removal of fluid after inducing fracture. CO_2 -SVFFs reduce the amount of water needed to make VES fluids by combining a small quantity of water with a large volume of CO_2 . The good viscoelastic properties of CO_2 -SVFFs are exhibited essentially for proppant transport. The inclusion of inorganic salt ions shows that the fluids have salinity tolerance with a moderate reduction in zero-shear viscosity. CO_2 is a relatively inexpensive trigger that is easy to remove and does not accumulate or contaminate waste streams.

The CO₂-SVFF has high shear tolerance, thermal stability, moderate salinity tolerance, and reduced core damage features. For gel breaking performance at 90 °C, the mixing of kerosene/standard brine with different proportions in CO₂-SVFFs results in a more

remarkable ability to lower the viscosity as per the standard of fracturing fluids (\leq 5 mPa·s for nearly 2 h). Increase in pressure of CO₂-SVFF, the rheological coefficient (k') and effective viscosity (ne) increased, but the rheological index (n') decreased. For higher temperatures (\geq 120 °C) and strong salinity formations (exceeding 2% CaCl₂, 3% NaCl, and MgCl₂), CO₂-SVFF with a low concentration of nanoparticles (NPs-CO₂-SVFF) is recommended to apply. Many studies focus on the laboratory scale; thus, researchers should evaluate the assessment of CO₂-SVFF for fracturing in numerous oilfields.

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