Synthesis and Properties of Exceptionally Thermo-Switchable Viscoelastic Responsive Zwitterionic Gemini Surfactants in Highly Saline Water

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ABSTRACT: Viscoelastic surfactants (VESs) have significant importance for stimulation of low-permeable reservoirs and acid diversion applications to effectively enhance hydrocarbon productivity. VESs offer lower residues, complete gel production, and lower formation damage that make them suitable candidates for hydraulic fracturing applications. In this research work, the synthesis of two new zwitterionic gemini surfactants 1 and 2 together with previously known amidosulfobutaine (C_{18}AMP3SB) has been achieved. Evaluation of viscosity behavior of neat surfactants in CaCl₂ solutions at varied temperatures and shear rates did not show any upsurge in their viscosities. Nevertheless, a mixture of surfactants 1 and 2 in combination with C_{18}AMP3SB displayed a significant increase in viscosity, transforming the solution into a highly viscous gel. At a fixed shear rate of 35 s⁻¹ and under different temperatures, solutions of the mixture of surfactants 1 and C_{18}AMP3SB displayed viscosities ranging from 4.34 to 354.3 cPs (81-fold enhancement). Likewise, viscosities of formulations based on mixing 2 and C_{18}AMP3SB under identical experimental conditions ranged from 3.89 to 290 cPs (74-fold enhancement). The viscofying stability tests at 90 °C at a shear rate of 35 s⁻¹ of mixed surfactant formulations revealed no appreciable change in their viscosities for up to 1 h. Moreover, temperature-dependent experiments suggested an increase in the viscosity with an increase in temperature. Thermogravimetric analysis revealed that these surfactants are thermally stable, with no appreciable loss of mass up to 300 °C. The viscoelastic properties of these surfactants suggest their potential and utility in well stimulation for enhanced oil recovery.

1. INTRODUCTION

Well-stimulation techniques have been widely applied to stimulate carbonate and sandstone reservoirs that allow an improved flow of hydrocarbons from the drainage area into the wellbore. Matrix stimulation and hydraulic fracturing treatments are the two main groups of stimulation treatments. Limestone formations or carbonate-bearing sandstone contains immense hydrocarbon reservoirs. In carbonate rocks, the matrix stimulation technique is employed wherein an acidic fluid is injected into a formation that leads to dissolution of carbonate minerals, resulting in the generation of new wormholes or channels. Nevertheless, for a better outcome, the smallest volume of acid with an optimum injection rate at a pressure lower than the fracturing pressure that can create a full wormhole formation is crucial. Moreover, proper placement of acid is also important for effective stimulation of the target zone. However, acid tendency to flow mainly into the most permeable zones as well as difference in wettability, wherein the acid-carbonate rock reaction is faster in water-saturated zones compared to oil-saturated rocks, makes the use of acid treatment problematic. Consequently, diverting agents are employed to plug temporarily the high permeability layers, which facilitate acid fluid to divert to the untreated areas in the reservoir, resulting in homogeneous acidizing and thereby dissolving the rock to create a pathway for hydrocarbon flow.
production.  

Polymer-based viscoelastic fluids have been frequently used in matrix acidification.  

Nevertheless, these diverters suffer from limitations such as colmatation of the bottom-hole formation zone and increasing the viscosity of the acid, which in turn leads to reducing the mass-transfer coefficient required for high-conductivity channel stimulation.

On the other hand, fracturing treatment is performed above the fracture pressure of the reservoir formation in order to induce a highly conductive flow path between the reservoir and the wellbore that in turn stimulates the flow of oil or gas. Fracturing fluids are mainly water-based fluids that may also contain proppants such as sand (“frac sand”) or ceramic beads. Fracturing fluids are mainly water-based fluids that may also contain proppants such as sand (“frac sand”) or ceramic beads. The viscosity of such chemical mixtures should be good enough to induce fracture geometry in the formation rock and to transport solid proppants into the fractures. The essential components of a fracturing fluid possess a specially designed synthetic polymer, a gelling agent (metal crosslinkers such as a zirconium complex), a multi-functional and environmentally friendly additive, and an oxidizing breaker. Nevertheless, the timings of the crosslinking of the system need to be appropriate and well-controlled. The stability of the fluid at high temperatures is another challenge that needs to be tackled.  

Guar and its synthetic derivatives have been frequently used for fracturing wells owing to their cost-effectiveness and good performance. Nevertheless, the upper limit of temperature for guar to be used as a polymer gel is 360 °F, and above this temperature, the formation has to be cooled down. In addition, a large loading of the polymer is also required. Moreover, although these fluids recover their viscosity after shear, they tend to lose a significant portion of their viscosity under high pressures.

Viscoelastic surfactants (VESs) bearing viscoelastic characteristics in aqueous solutions have been frequently used for upstream oil and gas applications for gravel completion and fracturing packs since 1995. In comparison to polymer-based fracturing fluids, VES-based systems have the advantages of low residue, complete gel breaking, and low formation damage and, as a result, enhance the production from the hydraulic fracturing reservoirs. Furthermore, VESs can also be employed for matrix acidification to improve the productivity and injectability of drilling in carbonate reservoirs.  

The chemical structures of VESs are similar to conventional surfactants that contain both hydrophilic and hydrophobic chains but with remarkable viscoelastic characteristics. The viscoelastic properties of these molecules are due to the formation of wormlike micelles, the entangled structures, via hydrophobic interactions, electrostatic interactions, and hydrogen bonding in aqueous solutions. The unique molecular structures of the surfactants drive them to self-assemble into various forms such as micelles, vesicles, and liquid crystals to reduce the area of interaction. The wormlike micelles have attracted a great deal of attention for fundamental research and industrial applications because of their unusual viscoelastic properties. In particular, switching the viscoelasticity of wormlike micelles through changes in the external medium has gained a great focus in chemical enhanced oil recovery (eOR). A diverse number of stimuli such as light, magnetic field, pH, CO2, redox conditions, and temperature have been explored to study the impact on the viscoelasticity behaviors of wormlike micelles. The thermos-triggered hydrogelation process is considered to be responsible for the temperature-based viscoelastic properties of wormlike micelles. During the heat-induced hydrogelation, a decrease in the solubility of hydrophobic moieties at elevated temperatures was observed. This suggests that heating decreases the solubility of hydrophobes, which in turn results in the creation of network gels.

We have recently reported an amidosulfobetaine-based zwitterionic surfactant (C18AMP3SB) for acid diversion applications. C18AMP3SB exhibited an apparent viscosity of 102 cPs in 20% NaCl solution under a shear rate of 85 s⁻¹, with an increase in temperature from room temperature to 90 °C. Likewise, the gemini surfactants have shown improved rheological properties due to their lower critical micelle concentration (CMC) and larger surface activity. Friesen et al. utilized gemini cationic surfactants that maintained 50 cPs at 250 °F under a shear rate of 100 s⁻¹. Moreover, Pal et al. also studied the rheological behavior of similar surfactants. In addition, a novel non-ionic gemini surfactant, derived from sunflower oil, was synthesized that exhibited promising self-aggregation ability. Similarly, Zhang et al. reported a self-diverting acid-gemini sulfonated surfactant (SDA-GS) that was made from the reaction of oleylamidopropyl dimethilamine, 1,3-propanesulfonate, and 2,2-bis(bromomethyl)propane-1,3-diol. The viscosity of SDA-GS was determined in the presence of CaCl2 and HCl. Recently, Wang et al. designed a hooked gemini viscoelastic surfactant (HGVES), with a CMC of 7.69 × 10⁻⁵ mol/mL that displayed a good viscoelastic behavior and fracturing performance. With a similar rheological characteristics like pseudoplastic fluids, 2 wt % of HGVES showed a core damage permeability of 5.35% without leaving behind any residue during the gel breaking process.

It has been well understood that sulfobetaine and hydroxyl sulfobetaine act as stabilizers in self-diverting acids. The existence of a sulfonate pattern is believed to be associated with the formation of wormlike micelles and can offer lower concentrations required for CMC.  

In our recent work, we have demonstrated that the nominal apparent viscosity of zwitterionic gemini surfactants in CaCl2 solution at 90 °C was significantly enhanced (up to ~10-fold) when mixed with C18AMP3SB. In view of the above, we have synthesized piperazine-based surfactants 1 and 2. The long hydrophobic chain containing the zwitterionic surfactant C18AMP3SB was also synthesized based on the previously reported procedures. At a fixed shear rate (35 s⁻¹) and under different temperatures, formulations based on solutions of the mixture of surfactants 1 or 2 with C18AMP3SB displayed an upsurge in viscosity, up to 81-fold enhancement. Herein, we wish to report the synthesis, spectroscopic characterization, apparent viscosity, and stability of time vs apparent viscosity of these surfactants.

2. MATERIALS AND METHODS

2.1. Materials and Instruments. Stearic acid (reagent grade, 95%, Sigma Aldrich), 1,3-propanesultone (≥99%, Sigma Aldrich), 3-(dimethylamino)-1-propylamine (99%, Sigma Aldrich), 1,4-butanetone (≥99%, Sigma Aldrich), piperazine (99%, Sigma Aldrich), CaCl2 (anhydrous, powder, 99.99%, Sigma Aldrich), acetone (≥99.8%, Honeywell), ethyl acetate (≥99.5%, Honeywell), diethyl ether (≥99.5%, Honeywell), methanol-d4 (99 atom % D, Sigma Aldrich), D2O (99.9
atom % D, Sigma Aldrich), and CDCl₃ (99.8 atom % D, Sigma Aldrich) were purchased and used as received. Before each experiment, the fresh stock solutions of anhydrous CaCl₂ (10–30%) were prepared in deionized water. The final products of VES molecules and the intermediates were characterized by ¹H-NMR and ¹³C-NMR on a 400 MHz Bruker spectrometer (AVANCE III) using TMS as an internal solvent by dissolving samples in deuterated solvents. The functional groups were ascertained by an FT-IR spectrophotometer (Perkin Elmer 16F PC, Perkin Elmer Inc. USA). The apparent viscosities of different VES formulations were determined using a Brookfield Rheometer DV3T linked with a programmable temperature controller (Ametek, USA). Thermogravimetric analysis (TGA) was performed to assess the thermal stability of the final products using an SDT Q600 (V20.9 Build 20) thermal analyzer.

2.2. Synthesis of Surfactants. 2.2.1. Synthesis of Surfactants 1 and 2. 2.2.1.1. Synthesis of 3,3’,3″-(Piperazine-1,4-diium-1,1,4,4-tetrayl)tetrakis(propane-1-sulfonate) (1). To a solution of piperazine 3 (1.0 g, 11.60 mmol) in ethyl acetate (20 mL) in a clean and dried round-bottom flask was added 1,3-propane sultone 4 (8.50 g, 69.66 mmol) and the reaction mixture was refluxed overnight at 95 °C. The white precipitates formed were filtered by using Whatman’s filter paper (grade 40), and the solid was sequentially washed with ethyl acetate (50 mL), diethyl ether (50 mL), and acetone (60 mL) to remove the unreacted starting materials.

The product was then dried under vacuum to afford the desired product 1 as a white solid (77%). ¹H-NMR [D₆] = δ 2.10 (m, 8H), 2.91 (t, 8H), 3.24 (t, 8H), 3.51 (t, 8H); ¹³C NMR [D₆] = δ 20.23, 48.36, 49.82, 56.11. FT-IR (cm⁻¹) = 2978, 1447, 1239, 1215, 1144, 953, 788.

2.2.2. Synthesis of 4,4′,4″,4‴-(Piperazine-1,4-diium-1,1,4,4-tetrayl)tetrakis(butane-1-sulfonate) (2). Based on the procedure adopted for the synthesis of surfactant 1, the title surfactant 2 was synthesized from the reaction of piperazine 3 and 1,4-butanediolic sultone 5 as a white solid (74%). ¹H-NMR [D₂O] = δ 1.71 (m, 8H), 2.85 (t, 8H), 3.12 (t, 8H), 3.32 (t, 8H), 3.66 (t, 8H); ¹³C NMR [D₂O] = δ 21.26, 23.43, 48.36, 49.82, 56.11. FT-IR (cm⁻¹) = 2993, 2962, 2832, 1627, 1473, 1352, 1210, 1138, 1029, 793.

2.2.3. Synthesis of the Zwitterionic Surfactant (C₁₈AMP3SB). The synthesis of C₁₈AMP3SB was accomplished as per our earlier reported procedures.³

2.3. Viscosification Experiments. The fresh stock solutions of anhydrous CaCl₂ in deionized water w/w% (10, 20, and 30%) were prepared. The synthesized surfactants 1, 2, and C₁₈AMP3SB (5% wt/wt) were mixed separately with stock CaCl₂ solutions (95% wt/wt). Afterward, surfactant 1 or 2 was used in combination with C₁₈AMP3SB in 1:1 in the stock CaCl₂ solutions (10, 20, and 30% w/w in deionized water). The apparent viscosities of the surfactants in CaCl₂ solutions was measured using a Brookfield Rheometer DV3T linked with thermosel through a programmable temperature controller (Ametek, USA) at ambient temperature, 40 °C, and at 90 °C under different shear rates (1–35 s⁻¹).

3. RESULTS AND DISCUSSION

3.1. Synthesis and Characterization of Surfactants. The piperazine-based surfactants 1 and 2 were synthesized as illustrated in Scheme 1. Condensation of piperazine 3 with 1,3-propane sultone 4 or 1,4-butanediolic sultone 5 in refluxing ethyl acetate provided the desired products 1 (77%) and 2 (74%), respectively.

Likewise, synthesis of C₁₈AMP3SB was achieved, as illustrated in Scheme 2. Refluxing neat stearic acid 6 with diamine 7 afforded 8, which was condensed with sultone 4 to yield the desired C₁₈AMP3SB.³

The chemical structures of the synthesized surfactants were ascertained by ¹H-NMR, ¹³C-NMR, and FT-IR (Figures S1–S3). The ¹H-NMR of surfactant 1 exhibited three triplets at δ 2.10 (−CH₂=CH₂CH₂SO₃⁻), 2.91 (−CH₂=CH₂CH₂SO₃⁻), and 3.24 (−(R₃)N⁺−CH₂=CH₂SO₃⁻) due to the propane sulfonate moiety. In addition, the spectrum displayed a triplet at δ 3.51 due to piperazine methylene protons attached to quaternized nitrogen. Similarly, the FT-IR spectrum of 1 exhibited two diagnostic peaks due to the S=O stretching at 1447 and 1239 cm⁻¹ and peaks at 2978 cm⁻¹ owing to the aliphatic C–H stretching. Likewise, the ¹H-NMR of surfactant 2 showed a similar peak pattern to that of 1, albeit slightly downfield shifted signals, together with an additional multiplet at δ 1.71. The FT-IR spectrum of 2 also revealed a similar peak pattern to that of 1, peaks due to the S=O stretching at 1473 and 1210 cm⁻¹ and aliphatic C–H stretching bands at 2993 and 2962 cm⁻¹.

The thermal stability of surfactants 1 and 2 was ascertained by thermogravimetric analysis (TGA). In these analyses, samples were heated from room temperature to 700 °C at a rate of 10 °C/min rise and purging nitrogen at a rate of 50 mL/min. As evident from Figure 1, these surfactants demonstrated high thermal stability and showed no appreciable loss of mass up to 300 °C. Surfactants 1 and 2 showed the onset of decomposition temperatures (Td) at 350 and 362 °C, respectively. An abrupt weight loss above Td was realized that indicated the decomposition of surfactants (Figure 1).

3.2. Viscoelastic Behavior of Piperazine-Based Surfactants in Combination with C₁₈AMP3SB. The viscosity behavior of neat surfactants 1 and 2 was studied in CaCl₂ solutions, having different concentrations (10–30%) and varied temperatures (RT to 90 °C) at varying shear rates (1–35 s⁻¹). Under these experimental conditions, none of the surfactants exhibited any appreciable enhancement in their viscosities. However, formulations based on the mixture of surfactants 1 or 2 with C₁₈AMP3SB (1:1) under identical experimental conditions displayed a significant increase in viscosity (Tables 1 and 2).

The mixed surfactant formulation-based experiment resulted in a highly viscous gel-like material, as illustrated in Figure 2. Moreover, these results indicated a trend in a decrease in viscosity with increasing shear rate, which suggested that the solutions containing the mixture of C₁₈AMP3SB and gemini surfactants were non-Newtonian fluids in nature. In addition, the mixture of 1 and 2 each in combination with C₁₈AMP3SB...
in CaCl₂ solutions demonstrated a better shear rate resistance, which suggested that the calcium ions encourage the formation of wormlike micelles (rod-shaped micelles). For instance, the mixture of surfactant 1 with C₁₈AMP3SB (1:1) showed quite a higher enhancement in viscosity. At a fixed shear rate of 35 s⁻¹ and under different temperatures, i.e., ambient temperature, 40 °C, and 90 °C, the mixture in 10% CaCl₂ solution displayed viscosities ranging from 4.34 to 354.3 cPs (81-fold enhancement). Likewise, in 20% CaCl₂ solution, the viscosity varied from 3.89 to 209.9 cPs, and for 30% CaCl₂ solution, it was from 6.38 to 54.69 cPs (Figure 3).

Similarly, the mixture of surfactant 2 with C₁₈AMP3SB (1:1 wt/wt) at a fixed shear rate of 35 s⁻¹ and under different temperatures, i.e., ambient temperature, 40 °C, and 90 °C, with 10% CaCl₂ solution showed viscosities in the range from 4.34 to 167.8 cPs (74-fold enhancement); for 20% CaCl₂ solution, the viscosity varied from 3.89 to 290 cPs and that for 30% CaCl₂ solution was 6.38 to 33.47 cPs (Figure 4).

### 3.3. Effect of Temperature on the Viscosity

The temperature dependence of these VES formulations was also investigated over a temperature range of ambient to 90 °C. It was assumed that the rise in the temperature would lead to an increase in the thermal motion of the molecules, which can

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**Table 1. Viscosification Results of Surfactant 1 in Combination with C₁₈AMP3SB**

| shear rate | 1−5% + C₁₈AMP3SB-5% + CaCl₂(10%)-90% | 1−5% + C₁₈AMP3SB-5% + CaCl₂(20%)-90% | 1−5% + C₁₈AMP3SB-5% + CaCl₂(30%)-90% |
|-----------|-------------------------------------|-------------------------------------|-------------------------------------|
|           | RT 40 °C 90 °C                      | RT 40 °C 90 °C                      | RT 40 °C 90 °C                      |
| 1.02      | 24.32 7.81 6047                     | 15.23 15.76 2891                   | 7.97 7.67 62.56                    |
| 5.00      | 7.64 4.33 1374                      | 10.33 7.91 733.4                   | 7.97 4.83 62.02                    |
| 10.00     | 6.56 3.19 742.4                     | 7.28 6.32 411.8                    | 7.81 4.78 60.13                    |
| 15.00     | 6.12 3.12 510.5                     | 6.54 5.47 292.2                    | 6.91 4.57 57.34                    |
| 20.00     | 5.37 2.87 393.9                     | 5.18 4.56 243.5                    | 6.83 4.38 55.41                    |
| 25.00     | 4.78 2.79 380.2                     | 4.67 4.09 232.7                    | 6.71 4.25 55.03                    |
| 35.00     | 4.34 1.61 354.3                     | 3.89 3.9 209.9                     | 6.38 3.83 54.69                    |

**Table 2. Viscosification Results of Surfactant 2 in Combination with C₁₈AMP3SB**

| shear rate | 2−5% + C₁₈AMP3SB-5% + CaCl₂(10%)-90% | 2−5% + C₁₈AMP3SB-5% + CaCl₂(20%)-90% | 2−5% + C₁₈AMP3SB-5% + CaCl₂(30%)-90% |
|-----------|-------------------------------------|-------------------------------------|-------------------------------------|
|           | RT 40 °C 90 °C                      | RT 40 °C 90 °C                      | RT 40 °C 90 °C                      |
| 1.02      | 24.32 23.44 234.4                   | 15.23 7.81 403.4                   | 7.97 12.33 54.7                    |
| 5.00      | 7.64 4.78 192.9                     | 10.33 4.78 390.6                   | 7.97 9.27 35.08                    |
| 10.00     | 6.56 3.72 188.1                     | 7.28 4.1 370.6                     | 7.81 8.66 35.06                    |
| 15.00     | 6.12 3.64 185.4                     | 6.54 3.72 342.6                    | 6.91 7.16 34.67                    |
| 20.00     | 5.37 3.29 181.7                     | 5.18 3.59 318                      | 6.83 6.54 34.53                    |
| 25.00     | 4.78 3.19 178.5                     | 4.67 3.19 298                      | 6.71 5.33 34.11                    |
| 35.00     | 4.34 2.87 167.8                     | 3.89 2.87 290                      | 6.38 4.97 33.47                    |
cause the network microstructure of viscoelastic surfactants to transform into single wormlike micelles. Moreover, plots of Figures 3 and 4 showed that at higher temperatures, these surfactants exhibited a higher viscosity at lower shear rates and further the viscosity reduced with an increase in shear rate. This suggested that the initial rise in viscosity with temperature in a non-Arrhenius pattern was due to predominance of van der Waals forces that facilitated the growth of wormlike micelles. However, in the higher shear rate region, viscosity decreases with temperature because of the reduced cohesion of surfactant molecules. Therefore, the neat mixtures of C18AMP3SB with surfactants 1 and 2 in a varied concentration of CaCl2 solutions (10–30%w/w) exhibited an increase in viscosity with an increase in temperature from ambient to 90 °C (Figure 5).

3.4. Stability of Viscosified Formulations. From all the formulations of VES molecules made for surfactants 1 and 2 in combination with C18AMP3SB using CaCl2 solution (10–30%), 1 with C18AMP3SB in 10% CaCl2 solution and 2 with C18AMP3SB in 20% CaCl2 solution exhibited the best results (Table 1 and Figures 3 and 4). Therefore, these two formulations were subjected to their viscofying stability test at 90 °C under a shear rate of 35 s⁻¹ for 1 hour. These results showed that the apparent viscosities of these formulations remained stable and did not show a significant change. Moreover, it also confirms that these VES formulations are stable at high temperatures and high shear rates. However, a small change in the viscosity approximately up to 5% was observed. This insignificant change in viscosity might be due to variation in concentrations of the samples incurred due to vaporization of water because the stability test of viscosification was performed in an open system for a longer period (Figure 6). The stability of VES formulations at a high temperature and shear rate suggested that the wormlike structures remain intact from a higher shear stress and temperature for a longer period of time.

3.5. Gel Breaking Properties of Piperazine-Based Surfactants 1 and 2 in Combination with C18AMP3SB. The gel-breaking properties of neat surfactants 1 and 2 and their mixtures with C18AMP3SB were studied by mixing them...
with diesel, from 1.37 to 21.76%, in the presence of 20% CaCl$_2$ solution (Table 3).

The mixture of surfactant 1 and C$_{18}$AMP3SB (1:1 w/w) displayed a decline in the apparent viscosity up to 21.76% after the addition of diesel (Figure 7a). Similarly, the gel breaking of the mixture of surfactant 2 and C$_{18}$AMP3SB (1:1 w/w) was decreased from 10.02% and then starts increasing (Figure 7b).

4. CONCLUSIONS

In conclusion, two new zwitterionic gemini surfactants 1 and 2 and a previously known amidosulfobutaine (C$_{18}$AMP3SB) have been synthesized. Although formulations based on solutions of individual surfactants 1 and 2 in aqueous CaCl$_2$ did not show any upsurge in their viscosities, formulations based on solutions of the mixture of 1 and 2 in combination with C$_{18}$AMP3SB exhibited enhancement in their viscosities to 81-fold and 74-fold, respectively. Moreover, at higher temperatures, these surfactants exhibited a higher viscosity at lower shear rates and the viscosity diminished with an increase in shear rate. This suggested that the initial rise in viscosity with temperature in a non-Arrhenius pattern was due to predominance of van der Waals forces that facilitated growth of wormlike micelles. However, in the higher shear rate region, a decrease in viscosity with an increase in temperature was linked to reduced cohesion of surfactant molecules. The high thermal stability of these surfactants, as revealed by TGA, coupled with the high viscofying stability of these surfactants hold great promise and potential for their use in well stimulation for the enhancement of oil recovery.

■ ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c03817.

(Figure S1) $^1$H-NMR and $^{13}$C-NMR of surfactant 1, (Figure S2) $^1$H-NMR and $^{13}$C-NMR of surfactant 2, and (Figure S3) $^1$H-NMR and $^{13}$C-NMR of surfactant C$_{18}$AMP3SB (PDF)

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Notes

The authors declare no competing financial interest.

■ REFERENCES

(1) YUAN, S.; WANG, Q. New Progress and Prospect of Oilfields Development Technologies in China. Pet. Explor. Dev. 2018, 45, 698–711.

(2) Nwoke, L. A. Development of Volumetric Horizontal Well Stimulation Model. In All Days; SPE, 2013. DOI: 10.2118/165143-MS.

(3) Mansha, M.; Ullah, N.; Kalgaonkar, R. A.; Baqader, N. Synthesis, Characterization, and Viscosification of Amidosulfobutaine and Zwitterionic Gemini Surfactants. J. Surfactants Deterg. 2021, 24, 697–706.

(4) Hoefner, M. L.; Fogler, H. S. Pore Evolution and Channel Formation during Flow and Reaction in Porous Media. AIChE J. 1988, 34, 45–54.

(5) Hoefner, M. L.; Fogler, H. S. Fluid-Velocity and Reaction-Rate Effects During Carbonate Acidizing: Application of Network Model. SPE Prod. Eng. 1989, 4, 56–62.

(6) Bulgakov, G. T.; Kharisov, R. Y.; Sharifullin, A. R.; Pestrikov, A. V. Modeling and Optimizing the Design of Matrix Treatments in Carbonate Reservoirs with Self-Diverting Acid Systems. J. Phys.: Conf. Ser. 2015, 574, No. 012070.

(7) Buijse, M. A.; Glasbergen, G. A Semi-Empirical Model To Calculate Wormhole Growth in Carbonate Acidizing. In SPE Annual Technical Conference and Exhibition; SPE, 2005. DOI: 10.2118/96892-MS.

(8) Kallayayan, L. J.; Martin, A. N. The Art and Practice of Acid Placement and Diversion: History, Present State, and Future. In SPE Annual Technical Conference and Exhibition; SPE, 2009. DOI: 10.2118/124411-MS.

(9) Lynn, J. D.; Nasr-El-Din, H. A. Core Based Comparison Of The Reaction Characteristics Of Emulsified And In-Situ Gelled Acids In Low Permeability, High Temperature, Gas Bearing Carbonates. In All Days; SPE, 2001. DOI: 10.2118/65386-MS.

(10) Nasr-El-Din, H. A.; Al-Humaidan, A. Y.; Fadhel, B. A.; Frenier, W. W.; Hill, D. Investigation of Sulfide Scavengers in Well Acidizing Fluids. In SPE International Symposium on Formation Damage Control; SPE, 2000. DOI: 10.2118/58712-MS.

(11) Fink, J. Petroleum Engineer’s Guide to Oil Field Chemicals and Fluids; 3rd Ed.; Gulf Professional Publishing, 2021.

(12) Gupta, D. V.; Carman, P. Fracturing Fluid for Extreme Temperature Conditions Is Just as Easy as the Rest. In SPE Hydraulic Fracturing Technology Conference; SPE, 2011. DOI: 10.2118/140176-MS.

(13) Stewart, B. R.; Mullen, M. E.; Howard, W. J.; Norman, W. D. Use of a Solids-Free Viscous Carrying Fluid in Fracturing Applications: An Economic and Productivity Comparison in Shallow Completions. In SPE European Formation Damage Conference; SPE, 1995. DOI: 10.2118/30114-MS.

(14) Brown, J. E.; King, L. R.; Nelson, E. B.; Ali, S. A. Use of a Viscoelastic Carrier Fluid in Frac-Pack Applications. In SPE European Formation Damage Conference; SPE, 1996. DOI: 10.2118/31114-MS.

(15) Nehmer, W. L. Viscoelastic Gravel-Pack Carrier Fluid. In SPE Formation Damage Control Symposium; SPE, 1988. DOI: 10.2118/17168-MS.

(16) Hull, K. L.; Sayed, M.; Al-Muntasher, G. A. Recent Advances in Viscoelastic Surfactants for Improved Production From Hydrocarbon Reservoirs. SPE J. 2016, 21, 1340–1357.

(17) Chang, F. F.; Accock, A. M.; Geoghagan, A.; Huckabee, P. T. Experience in Acid Diversion in High Permeability Deep Water Formations Using Visco-Elastic-Surfactant. In SPE Annual Technical Conference and Exhibition; SPE, 2001. DOI: 10.2118/71691-MS.

(18) Yu, M.; Nasr-El-Din, H. A. Quantitative Analysis of Viscoelastic Surfactants. In SPE International Symposium on Oilfield Chemistry; SPE, 2009. DOI: 10.2118/121715-MS.

(19) Li, K.; Jing, X.; He, S.; Ren, H.; Wei, B. Laboratory Study Displacement Efficiency of Viscoelastic Surfactant Solution in Enhanced Oil Recovery. Energy Fuels 2016, 30, 4467–4474.

(20) Rosen, M. J. Surfactants and Interfacial Phenomena; 3rd Ed.;; 2004.

(21) Dress, C. A. Wormlike Micelles: Where Do We Stand? Recent Developments, Linear Rheology and Scattering Techniques. Soft Matter 2007, 3, 956–970.

(22) Qin, W.; Yue, L.; Liang, G.; Jiang, G.; Yang, J.; Liu, Y. Effect of Multi-Walled Carbon Nanotubes on Linear Viscoelastic Behavior and Microstructure of Zwitterionic Wormlike Micelle at High Temperature. Chem. Eng. Res. Des. 2017, 123, 14–22.

(23) Yang, D.; Zhao, J. A Light-Responsive Organofluid Based on Reverse Worm-like Micelles Formed from an Equi-Charged, Mixed, Anionic Gemini Surfactant with an Azobenzene Spacer and a Cationic Conventional Surfactant. Soft Matter 2016, 12, 4044–4051.

(24) Kelly, E. A.; Houston, J. E.; Evans, R. C. Probing the Dynamic Self-Assembly Behaviour of Photoswitchable Wormlike Micelles in Real-Time. Soft Matter 2019, 15, 1253–1259.

(25) Pletneva, V. A.; Molchanov, V. S.; Philippova, O. E. Viscoelasticity of Smart Fluids Based on Wormlike Surfactant Micelles and Oppositely Charged Magnetic Particles. Langmuir 2015, 31, 110–119.

(26) Chen, R.; Zhuang, G.-L.; Wang, Z.-Y.; Gao, Y.-J.; Li, Z.; Wang, C.; Zhou, Y.; Du, M.-H.; Zeng, S.; Long, L.-S.; et al. Integration of Bio-Inspired Lanthanide-Transition Metal Cluster and P-Doped Carbon Nitride for Efficient Photocatalytic Overall Water Splitting. Natl. Sci. Rev. 2021, 8, nwa234.

(27) Ye, S.; Zhai, Z.; Shang, S.; Song, Z. PH-Induced Hydrogels and Viscoelastic Solutions Constructed by a Rosin-Based Pseudo-Gemini Surfactant. J. Mol. Liq. 2022, 361, No. 119445.

(28) Zhang, Y.; Feng, Y.; Wang, J.; He, S.; Guo, Z.; Chu, Z.; Dreiss, C. A. CO2-Switchable Wormlike Micelles. Chem. Commun. 2013, 49, 4902–4904.

(29) Zhang, Y.; Yang, C.; Guo, S.; Chen, H.; Liu, X. Tandem Triggering of Wormlike Micelles Using CO2 and Redox. Chem. Commun. 2016, 52, 12717–12720.

(30) Zhang, Y.; Kong, W.; Wang, C.; An, P.; Fang, Y.; Feng, Y.; Qin, Z.; Liu, X. Switching Wormlike Micelles of Sulfonate-Containing Surfactant Using Redox Reaction. Soft Matter 2015, 11, 7469–7473.

(31) Zhang, Y.; Chen, Z.; Zhao, Y. Viscoelastic Micellar Solution Formed by a Self-Based Ionic Liquid Surfactant and Its Response to Redox Changes. Phys. Chem. Chem. Phys. 2019, 21, 14734–14744.

(32) Abdulaziz Alghamdi, O.; Mansha, M.; Kalanthoden, A. N.; Kamal, M. S.; Khan, M. Fracturing Fluid Applications of Carboxylate-terminated Linoleic Acid Surfactants for Improved Production From Shallow Carbonate Reservoirs. Colloid Interface Sci. Commun. 2022, 49, No. 100643.

(33) Pochan, D. J.; Schneider, J. P.; Kretzinger, J.; Ozbas, B.; Rajagopal, K.; Haines, L. Thermally Reversible Hydrogels via Intramolecular Folding and Consequent Self-Assembly of a de Novo Designed Peptide. J. Am. Chem. Soc. 2003, 125, 11802–11803.

(34) Morimoto, N.; Qiu, X.-P.; Winnik, F. M.; Akiyoshi, K. Dual Stimuli-Responsive Nanogels by Self-Assembly of Polysaccharides Lightly Grafted with Thiol-Terminated Poly(N-isopropylacrylamide) Chains. Macromolecules 2008, 41, 5985–5987.
(35) Chu, Z.; Feng, Y. Thermo-Switchable Surfactant Gel. *Chem. Commun.* 2011, 47, 7191.

(36) Li, Q.; Yue, X.; Shang, P.; Quan, Y.; Ren, M.; Ma, Y.; Chen, X. Environmental Stimuli Induced Phase Transition in the Aqueous Mixture Solution of Gemini Surfactants and Sodium Deoxycholate. *Colloids Surf., A* 2016, 489, 67–74.

(37) Xu, T.; Mao, J.; Zhang, Y.; Yang, X.; Lin, C.; Du, A.; Zhang, H. Application of Gemini Viscoelastic Surfactant with High Salt in Brine-Based Fracturing Fluid. *Colloids Surf., A* 2021, 611, No. 125838.

(38) Huang, F.; Pu, C.; Lu, L.; Pei, Z.; Gu, X.; Lin, S.; Wu, F.; Liu, J. Gemini Surfactant with Unsatuated Long Tails for Viscoelastic Surfactant (VES) Fracturing Fluid Used in Tight Reservoirs. *ACS Omega* 2021, 6, 1593–1602.

(39) Feng, J.; Liu, X.-P.; Zhang, L.; Zhao, S.; Yu, J.-Y. Dilational Viscoelasticity of the Zwitterionic Gemini Surfactants with Polyoxyethylene Spacers at the Interfaces. *J. Dispersion Sci. Technol.* 2011, 32, 1537–1546.

(40) Pal, N.; Saxena, N.; Mandal, A. Synthesis, Characterization, and Physicochemical Properties of a Series of Quaternary Gemini Surfactants with Different Spacer Lengths. *Colloid Polym. Sci.* 2017, 295, 2261–2277.

(41) Friesen, D.; Seymour, B.; Sanders, A. A Novel Gemini Cationic Viscoelastic Surfactant-Based Fluid for High Temperature Well Stimulation Applications. In *Day 3 Thu, September 23, 2021*; SPE, 2021. DOI: 10.2118/206297-MS.

(42) Pal, N.; Saxena, N.; Mandal, A. Studies on the Physicochemical Properties of Synthesized Tailor-Made Gemini Surfactants for Application in Enhanced Oil Recovery. *J. Mol. Liq.* 2018, 258, 211–224.

(43) Pal, N.; Samanta, K.; Mandal, A. A Novel Family of Non-Ionic Gemini Surfactants Derived from Sunflower Oil: Synthesis, Characterization and Physicochemical Evaluation. *J. Mol. Liq.* 2019, 275, 638–653.

(44) Pal, N.; Kumar, N.; Verma, A.; Ojha, K.; Mandal, A. Performance Evaluation of Novel Sunflower Oil-Based Gemini Surfactant(s) with Different Spacer Lengths: Application in Enhanced Oil Recovery. *Energy Fuels* 2018, 32, 11344–11361.

(45) Zhang, W.; Mao, J.; Yang, X.; Zhang, H.; Yang, B.; Zhang, Z.; Zhang, Y.; Zhao, J. Development of a Stimuli-Responsive Gemini Zwitterionic Viscoelastic Surfactant for Self-Diverting Acid. *J. Surfactants Deterg.* 2019, 22, 535–547.

(46) Wang, C.; Qiu, G.; Long, X.; Wang, T.; Zhang, X.; Liang, L.; Bai, J.; Li, Z.; Qiu, L.; Yang, X.; et al. Hooked Gemini Viscoelastic Surfactant Based on Linolenic Oil for Oil Recovery and Its Various Gel-Breaking Mechanisms. *J. Pet. Sci. Eng.* 2021, 204, No. 108717.

(47) Wang, Y.; Zhang, Y.; Liu, X.; Wang, J.; Wei, L.; Feng, Y. Effect of a Hydrophilic Head Group on Krafft Temperature, Surface Activities and Rheological Behaviors of Erucyl Amidobetaines. *J. Surfactants Deterg.* 2014, 17, 295–301.

(48) Yang, J.; Hou, J. Synthesis of Erucic Amide Propyl Betaine Compound Fracturing Fluid System. *Colloids Surf., A* 2020, 602, No. 125098.

(49) Chu, Z.; Feng, Y. A Facile Route towards the Preparation of Ultra-Long-Chain Amidosulfobetaine Surfactants. *Synlett* 2009, 2009, 2655–2658.

(50) Mao, J.; Zhang, H.; Zhang, W.; Fan, J.; Zhang, C.; Zhao, J. Dissymmetric Beauty: A Novel Design of Heterogemini Viscoelastic Surfactant for the Clean Fracturing Fluid. *Ind. Eng. Chem. Res.* 2018, 60, 133–142.

(51) Dai, C.; Li, Y.; Xie, Q.; Xu, K.; Hu, Y.; Zhou, Z.; Wu, Y. Reduction of Clean Fracturing Fluid Filtration Loss by Viscosity Enhancement Using Nanoparticles: Is It Feasible? *Chem. Eng. Res. Des.* 2020, 156, 414–424.