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Synthesis, Characterization, and Viscosification of Amidosulfobutaine and Zwitterionic Gemini Surfactants

Muhammad Mansha¹ · Nisar Ullah¹ · Rajendra A. Kalgaonkar² · Nour Baqader²

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Abstract The viscoelastic surfactants (VES)-based acid diverters are frequently used to divert acid flow from highpermeability layers into low-permeability for enhanced overall productivity of the treated well. In general, an optimum VES-based system possesses advantages of decrease in absorption loss, damage of reservoir, and improved adaptability of active agents to high salinity. Herein, we report the synthesis of three new zwitterionic gemini surfactants (1-3) and previously known amidosulfobutaine (C₁₈AMP3SB) has been accomplished for the investigation of diverting acid performance. The synthesis of these surfactants was achieved by the amidation of the acid chlorides of commercially available fatty acids with 3-(dimethylamino)-1-propylamine followed by subsequent reactions with appropriate sultone ethyl or 4-bromobutanoate. The synthesized surfactants were well characterized by spectroscopic methods including IR and NMR spectroscopy. The thermogravimetric analysis (TGA) results suggested that surfactants (1-3) and C₁₈AMP3SB possess excellent thermal stability, with no appreciable loss of mass up to 300°C. The viscosity measurements of the neat surfactants (1-3) and C₁₈AMP3SB were performed under various temperatures, in the presence of different concentration of calcium chloride salt with the aid shear viscosimetry. The analysis revealed that the viscosity of

Muhammad Mansha manshachohan@kfupm.edu.sa

Nisar Ullah nullah@kfupm.edu.sa

neat C₁₈AMP3SB increases with increase in concentration of CaCl₂. With 10% CaCl₂ solution, the viscosity was increased from 7.5 to 33.55 cPs, whereas in 20% CaCl₂ the viscosity reached to 102 cPs with rise in temperature from ambient to 90°C. Moreover, the viscosity of neat surfactants (1–3) did not exhibit any appreciable viscosity change under the experimental conditions. However, the mixture of surfactants (1–3) each in combination with C₁₈AMP3SB (1:1) displayed significant upsurge in the viscosity, up to more than 10 folds.

Keywords Zwitterionic gemini surfactants · Viscoelastic surfactants · Heat stimuli response · Oil well stimulation

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Introduction

Crude oil is considered one of the most readily accessible sources of energy. It constitutes a crucial source of raw materials required for the chemical industries, on which daily life relies upon. Well stimulation techniques enable improved extraction of hydrocarbon reserves that the conventional recovery processes, such as gas or water displacement are unable to achieve. Matrix stimulation is one of the well stimulation techniques wherein an acidic fluid or solvent is injected into a formation at a pressure lower than the fracturing pressure. Carbonate rock acidification results in dissolution of carbonate minerals, producing new wormholes or channels that bypass damage. An optimum injection rate is required to attain a breakthrough with a full wormhole formation by smallest volume of acid. In addition, stimulation of the target zone requires proper

¹ Chemistry Department, King Fahd University of Petroleum & Minerals, Dhahran, 31261, Saudi Arabia

² Production Technology Division, EXPEC Advanced Research Center, Saudi Aramco, Dhahran, 31311, Saudi Arabia

placement of acid, which in turn depends upon a relatively close permeability ratio (Hoefner and Fogler, 1988, 1989). Nevertheless, studies have suggested that the effectiveness of acid treatment becomes limited because acid tends to flow primarily into the most permeable zones, leaving the rest of the reservoir pores unaffected or poorly affected by the acid. In addition, due to difference in wettability the reaction of acid with carbonate rocks in water-saturated zones is faster than that with oil-saturated rocks which leads to enhanced acid activity in water zones, resulting in their increased injectivities (Bulgakova et al., 2014). Therefore, acid diversion into low-permeability layers by limiting fluid flow into high-permeability layers would enhance the coverage of the acid exposure zone and result in the overall productivity of the treated well (Glasbergen and Buijse, 2006; Kalfayan and Martin, 2009). Polymer-based viscoelastic fluids have been frequently used as flow diverters (Kalfayan and Martin, 2009). However, these fluids suffer from limitation such as increasing the viscosity of the acid which in turn leads to decreasing injection rate. (Lynn and Nasr-El-Din, 2001; Nasr-El-Din et al., 2002, 2004b).

Viscoelastic-surfactant (VES)-based acids can offer solution to mitigate this problem (Nasr-El-Din et al., 2004a, 2006a). VES-based systems employ specialized surfactant that in acid solution forms spherical micelles when present above its critical micelles concentration (CMC). The stimulation of carbonate reservoir with hydrochloric acid leads to decrease in the pH (~ pH 2) and increase in the concentrations of calcium ions, which in turn force the surfactant monomers to form rod-shaped micelles. As a result, the viscosity of the fluid is significantly increased, which acts as a temporary barrier to divert acid into untreated lowpermeability zones. However, in the presence of highviscosity hydrocarbons and at slightly higher pH (pH 3–4), when processing is over, the high-viscosity barrier collapses (Taylor et al., 2003).

In the recent past, several studies attested the efficacy of VES-based system as acid diverters (Al-Ghamdi et al., 2010; Gomaa et al., 2012; Yu et al., 2010). Chang et al. have reported the use of carboxybetain VES as selfdiverting acid systems, which successfully diverted acid from high-permeability core into the low-permeability core (Al-Ghamdi et al., 2014). In another report, the addition of polyelectrolyte into self-diverting acid systems based on VES resulted in the increase in the thermal stability of the fluids. The rheological properties of the fluid were adjusted by customizing surfactant concentration, temperature, and pH of fluid. The application of self-diverting acid systems was successfully demonstrated in the oil producing wells without emulsion concerns (Alleman et al., 2003). In other studies, parallel flow tests were performed by deploying cationic VES (Nasr-El-Din et al., 2009) and amine oxide J Surfact Deterg

VES (Nasr-El-Din et al., 2006b). It was observed that the use of these self-diverting acid systems led to increased effluent volume through the lower-permeability core, which in turn allowed preferential acid breakthrough in the lowerpermeability core as compared to higher-permeability core. Likewise, carboxybetaine VES-based acid was used by Tardy et al. to develop the reactive flow of self-diverting acid. They suggested that wormhole penetration and zonal coverage are the most important characteristics of self-diverting acids. Moreover, the viscosity buildup in the matrix occurs around wormhole, which are virtually infinitely conductive (Al-Ghamdi et al., 2014). Similarly, Al-Ghamdi et al. also deployed carboxybetaine VES-based acid and concluded that the rate of acid injection is crucial to obtain the maximum acid diversion efficiency (Al-Ghamdi et al., 2014).

Similarly, sulfobetaine and hydroxyl sulfobetaine have been employed as thickeners in self-diverting acids. The sulfonate function is known to assist in rodlike micelles formation and also reduces the concentration required for CMC (Wang et al., 2014). On the other hand, the two hydrophilic groups in gemini surfactants permit water solubility, self-assembling properties, and tolerance for hard water (Kabir and Koya, 2010). Zhang et al., have recently developed a zwitterionic gemini surfactant to evaluate its acid diverting performance (Zhang et al., 2019).

Commonly used zwitterionic surfactants-based VES molecules are neutral in nature, due to the presence of equal number of positive and negative charges. Consequently, their adsorption to reservoir minerals is lower. However, under extreme acidic conditions protonation of anionic function of zwitterionic surfactant may result in cationic moiety and hence higher adsorption reservoir leads to to minerals (Holmberg, 2002). On the other hand, important structural characteristics features of zwitterionic gemini surfactants include large number of hydrophilic groups, which enabled them to self-assemble for their enhanced viscofication. The zwitterionic gemini surfactants enjoy the advantages of decreasing absorption loss, damage of reservoir, and improved adaptability of active agents to high salinity (Kamal, 2016; Raoul Zana, 2004). Through this research article, we report the synthesis and viscosification of new zwitterionic gemini surfactants (1-3) individually and in combination with zwitterionic surfactant (C₁₈AMP3SB).

Materials and Methods

Materials

All the chemicals like sebacic acid (99%), 3-(dimethylamino)-1-propylamine (99%), 1,3-propanesultone (≥99%), 1,4-butane sultone (\geq 99%), stearic acid (reagent grade, 95%), ethyl 4-bromobutyrate (95%), CaCl₂ (anhydrous, powder, 99.99%) were purchased from Sigma-Aldrich and used as received without further purifications. The stock solutions of CaCl₂ were prepared in deionized water. VES molecules and their intermediates were characterized by ¹H and ¹³C NMR on a 500 MHz spectrometer (JEOL JNM-LA, JEOL USA Inc.) and Infrared spectra on FTIR spectrophotometer (Perkin Elmer 16F PC, Perkin Elmer Inc. USA).

The viscosity of VES at different temperatures was recorded by a Brookfield Rheometer DV3T coupled with thermosel *via* programable temperature controller (Ametek, USA). Thermogravimetric analysis (TGA) was measured on SDT Q600 (V20.9 Build 20) thermal analyzer.

Synthesis of Surfactants

Synthesis of Gemini Surfactants

Synthesis of N^{1} , N^{10} -bis(3-(dimethylamino)propyl) decanediamide (**6**)

To a cold thionyl chloride (10 mL) at 0 °C was added sebacic acid 4 (5.0 g, 24.72 mmol) portion-wise with continuous stirring in the reaction flask. After completion of the addition, the temperature was slowly raised to room temperature and the stirring was continued overnight. The volatile was then evacuated under vacuum and the product acid chloride was taken in CH₂Cl₂ (50 mL) and cooled to 0 °C followed by the slow addition 3-(dimethylamino)-1-propylamine 5 (6.31 g, 61.8 mmol) and triethylamine (20.6 mL, 148 mmol). After completion of the addition, the stirring was continued overnight at room temperature. The volatiles were then evaporated under reduced pressure in rotary evaporator. The residues were triturated with methanol and the solid was filtered then dried under reduced pressure using rotary evaporator to get compound 6 as white solid (90%). ¹H NMR [CDCl₃] = δ 1.255–1.302 (m, 8H), 1.577 (m, 4H), 1.637 (t, 4H), 2.121 (t, 4H), 2.280 (s, 12H), 2.367 (t, 4H), 3.319 (t, 4H), 6.948 (b, NH). ¹³C NMR [CDCl₃] = δ 25.68, 26.14, 29.19, 36.89, 39.20, 45.38, 58.60, 173.04. FTIR $(cm^{-1}) = 3303.67, 2921.83, 2852.83, 2811.75, 1635.01,$ 1538.76, 1468.29, 1379.05, 1238.83, 1100.88, 1041.46, 830.65, 714.41. C₂₀H₄₂N₄O₂ (370.58): calcd.: C 64.82, H 11.42, N 15.12; found: C 63.99, H 11.59, N 14.82.

Synthesis of N,N'-((malonylbis(azanediyl))bis(propane-3,1-diyl))bis(4-ethoxy-N,N-dimethyl-4-oxobutan-1-aminium) (**10**)

To a solution of compound **6** (3 g, 8.1 mmol) in dry acetone (30 mL) was added 1-bromo ethyl butanoate **9** (3.45 g, 17.81 mmol) and the reaction was refluxed for 48 h. Upon completion of the reaction (TLC analysis), the acetone was evaporated under vacuum and the product was successively washed with n-hexane (20 mL) and diethyl ether (2 × 20 mL) and dried under vacuum in rotary evaporator to obtain the title compound **10** as white solid (85%). ¹H NMR [D₂O] = δ 1.28 (m, 8H), 1.56 (m, 4H), 1.90–1.99 (m, 8H), 2.15–2.41 (m, 12H), 3.08 (s, 12H), 3.21–3.30 (m, 12H). ¹³C NMR [CDCl₃] = δ 18.95, 22.14, 25.22, 28.11, 33.32, 35.68, 35.88, 44.02, 50.66, 61.57, 63.46, 177.53, 180.53. FTIR (cm⁻¹) = 3354.99, 3293.41, 2972.37, 2937.59, 1651.13, 1547.90, 1487.79, 1170.46, 1032.04, 727.08. C₂₅H₅₀ Br₂N₄O₆ (660.21): calcd.: C 45.32, H 7.61, N 8.46 found: C 44.64, H 8.03, N 8.30.

Synthesis of 4,4,16,16-tetramethyl-9,11-dioxo-4,8,12,16-tetraazanonadecane-4,16-diium-1,19 *disulfonate (1)*

To a solution of compound **6** (0.43 g, 1.17 mmol) in ethyl acetate (15 mL) 1,3-propane sultone **7** (0.48 g, 3.49 mmol) and the reaction was refluxed overnight. The solid formed was filtered, washed with plenty of ethyl acetate and diethyl ether, and then dried under vacuum in rotary evaporator to obtain surfactant **1** a white solid (Yield = 93%). ¹H NMR $[D_2O] = \delta 1.15-1.25$ (m, 8H), 1.44 (m, 4H), 1.87 (t, 4H), 2.07 (t, 4H), 2.11 (t, 4H), 2.82 (t, 4H), 2.97 (s, 12H), 3.14 (t, 4H), 3.20 (t, 4H), 3.35 (t, 4H). ¹³C NMR $[CDCl_3] = \delta 18.11$, 22.23, 225.24, 35.87, 47.15, 50.70, 61.85, 62.18, 177.56. FTIR (cm⁻¹) = 3303.34, 2927.54, 2844.68, 1669.76, 1555.30, 1486.92, 1479.07, 1156.97, 1024.45, 929.32, 794.55, 682.02. C₂₆H₅₄ N₄O₈S₂ (614.86): calcd.: C 50.79, H 8.85, N 9.11; found: C 50.42, H 9.05, N 8.90.

Synthesis of 5,5,17,17-tetramethyl-10,12-dioxo-

5,9,13,17-tetraazahenicosane-5,17-diium-

1,21-disulfonate (2)

Following same procedure adopted for the synthesis of 1, surfactant 2 was synthesized by the reaction of compounds 6 and 8 white solid (88%).

¹H NMR [D₂O] = δ 1.17–1.25 (m, 8H), 1.45 (m, 4H), 1.67 (t, 4H), 1.78 (t, 4H), 1.86 (t, 4H), 2.11 (t, 4H), 2.18 (t, 4H), 2.83 (t, 4H), 2.94 (s, 12H), 3.14–3.23 (m, 12H). ¹³C NMR [CDCl₃] = δ 20.82, 21.07, 22.23, 25.29, 28.18, 35.73, 35.91, 43.59, 49.94, 50.74, 61.70, 63.42, 177.55. FTIR (cm⁻¹) = 3300.66, 2919.72, 2854.78, 1666.74, 1550.05, 1496.05, 1469.57, 1176.17, 1038.42, 956.74, 795.33, 686.20. C₂₈H₅₈ N₄O₈S₂ (642.91): calcd.: C 52.31, H 9.09, N 8.71; found: C 51.80, H 9.25, N 8.57.

Synthesis of mono ((1-carboxylato-4,4,16,16-tetramethyl-9,11-dioxo-4,8,12,16-tetraazaicosan-4,16-diium-20-oyl) sodium(III)) monosodium monoxide (**3**)

To a solution of surfactant 10 (2.59 g, 3.42 mmol) MeOH (20 mL) was added a solution of NaOH (0.3 g 7.53 mmol



Scheme 1 Synthesis of zwitterionic gemini surfactants 1-3

in 3 mL H_2O) dropwise and the reaction mixture was stirred overnight at room temperature. Upon the completion of the reaction (TLC analysis), volatiles were removed

under vacuum in rotary evaporator and trituration of the resultant residues with diethyl ether yielded to desired surfactant **3** very light yellow solid (95%). ¹H NMR [D₂O] = δ



Scheme 2 Synthesis of amidosulfobetaine surfactant (C₁₈AMP3SB)





Fig 1 TGA curves of gemini surfactants (1-3) and C₁₈AMP3SB

1.11 (t, 6H), 1.14–1.16 (m, 8H), 1.43 (m, 4H), 1.85–1.89 (t, 8H), 2.10 (t, 4H), 2.36 (t, 4H), 2.95 (s, 12H), 3.11–3.18 (m, 12H), 4.03 (m, 4H) ¹³C NMR [CDCl₃] = δ 13.27, 17.41, 22.22, 25.26, 28.17, 30.05, 35.71, 35.85, 50.84, 61.46, 61.95, 62.68, 174.39, 177.48. FTIR (cm⁻¹) = 3381.46, 2915.11, 2884.58, 1728.47, 1651.86, 1486.84, 1376.99, 1181.46, 1033.89, 724.72. C₂₈H₅₄ Na₂O₆ (588.38): calcd.: C 57.12, H 9.25, N 9.52; found: C 56.67, H 9.43, N 9.75.

Synthesis of C₁₈AMP3SB

Synthesis of $C_{18}AMP3SB$ was achieved as per earlier reported procedures. The spectral data coincided with the previously reported material (Chu and Feng, 2009).



Fig 2 The apparent viscosity of the $C_{18}AMP3SB$ with CaCl₂ solutions (10%, 20%, and 30%) versus shear rate at different temperatures



Fig 3 The apparent viscosity of the $C_{18}AMP3SB \& 1$ (1:1) with CaCl₂ solutions (10%, 20%, and 30%) *versus* shear rate at different temperatures

Results and Discussion

Synthesis and Characterization of Zwitterionic Gemini Surfactants

The synthesis of zwitterionic gemini surfactants (1-3) was accomplished as outlined in Scheme 1. The synthesis of these surfactants required the preparation of the key intermediate **6**, which was synthesized by condensing diacid chloride, generated by the reaction of sebacic acid (**4**) with



Fig 4 The apparent viscosity of the $C_{18}AMP3SB$ and 2 (1:1) with CaCl₂ solutions (10%, 20%, and 30%) *versus* shear rate at different temperatures



Fig 5 The apparent viscosity of C18AMP3SB and 3 (1:1) with CaCl2 solutions (10%, 20%, and 30%) versus shear rate at different temperatures



Fig 6 Effect of temperature on viscoelastic surfactants at shear rate of 85 s⁻¹ in (a) CaCl₂-10% (b) CaCl₂-30% (c) CaCl₂-20%

thionyl chloride, with 3-(dimethylamino)-1-propylamine (5) in dichloromethane solvent in 90% yield.

Condensation of diamine (6) with 1,3-propanesultone (7) or 1,4-butanesultone (8) produced surfactants 1 and 2,

respectively. Similarly, reaction of **6** with 4-bromoethyl butanoate (**9**) in refluxing acetone yielded **10**, which was hydrolyzed under basic conditions to generate the desired surfactant **3** in 90% overall yield from **6** (Scheme 1).

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Fig 7 Stability test of viscosification for VES molecules in CaCl₂-20% at 90°C under shear rate of 85 $\rm s^{-1}$

Synthesis and Characterization of C₁₈AMP3SB

The synthesis of amidosulfobetaine surfactant 3-(dimethyl (3-stearamidopropyl)ammonio)-propane-1-sulfonate

(C₁₈AMP3SB) was achieved based on earlier reported procedures, as outlined in Scheme 2 (Chu and Feng, 2009). In brief, refluxing the mixture of neat stearic acid (11) with *N*,*N*-dimethyl-1,3-propanediamine (5) at 160°C for 16 h afforded the tertiary amine (12), which was then condensed with 1,3-propanesultone (7) in ethyl acetate to produce the desired surfactant C₁₈AMP3SB in 86% overall yield from 11. The spectral data matched with the earlier reported material (Chu and Feng, 2009).

The chemical structures of all the intermediates and the final surfactant products were confirmed by spectroscopic methods. For instance, FT-IR spectrum of intermediate **6** displayed the presence of -N-H stretch at 3303 cm^{-1} and amide carbonyl (-CH₂-C=O-NH) stretching at 1635 cm⁻¹. Similarly, the presence of methylene (-CH₂-) stretching bands (2915 cm^{-1} and 2884 cm^{-1}) and bending vibrations $(1468 \text{ cm}^{-1} \text{ and } 1379 \text{ cm}^{-1})$ suggested the presence of alkyl chains. Likewise, the ¹HNMR of intermediate **6** exhibited resonance at δ 3.30 due to the methylene protons attached to amide function (-CH₂-NH(C=O)-), which appeared at δ 3.30 and peaks for methyl protons attached to tertiary nitrogen $(-N(CH_3)_2)$ at δ 2.22 (Hussain et al., 2016). Moreover, the ¹³C NMR displayed peaks due to the presence of carbonyl carbon of amide at δ 173.05 and methylene carbon attached to amide function (-CH₂-NH(C=O)-) δ 58.60. The spectrum also showed peak for methyl carbons attached to tertiary nitrogen (-N(CH₃)₂) at δ 45.38. .

Similarly, the ¹H NMR spectra of surfactants (1–3) showed downfield shift for the methyl protons attached to the quaternary nitrogen ((R)₂N(CH₃)₂). The peak at δ 2.22 in **6** was shifted to between δ 2.90 and 3.069 in the case of surfactants (1–3). Moreover, ¹³C NMR spectra of surfactants (1–3) exhibited a clear shift for methylene carbons attached to quaternary nitrogen (-CH₂-N⁺(CH₃)₂-CH₂-), at between δ 61.81 and 63.50. Furthermore, peaks due to the carbonyl carbons of amide group were found at δ 177.05. In addition, surfactants (**3**) also displayed peak due to carbonyl carbon at δ 180.53.

Thermogravimetric Analysis of Surfactants

The thermal stability of VES molecules at high temperature is very important. The stability of these molecules was assessed by thermogravimetric analysis (TGA). TGA was performed on SDT Q600 (V20.9 Build 20) thermal analyzer. In these analyses, samples were heated from room temperature to 700°C at the rate of 10 °C min⁻¹ rise by purging nitrogen at a rate of 50 mL min⁻¹. As evident from Fig. 1, these surfactants demonstrated high thermal stability and showed no appreciable loss of mass up to 300°C. The surfactants (**1–3**) showed the onset of decomposition temperatures (T_d) at 320, 340, and 310°C, respectively. While the onset of decomposition temperature for C₁₈AMP3SB was observed at 355°C. An abrupt loss in weight above the T_d was realized that indicated the decomposition of the main chain of surfactants (Fig. 1).

Viscosification

The relationship of apparent viscosity of C₁₈AMP3SB and its mixture with gemini surfactants (1-3) each in different concentrations of CaCl₂ solutions (10-30%w/w) at varied temperatures (RT-90°C) with varying shear rates $(1-85 \text{ s}^{-1})$ was studied. The amidosulfobetaine surfactant C₁₈AMP3SB showed significant changes in its apparent viscosity in CaCl₂ solutions (10, 20, and 30%w/w) at varied temperature (RT-90°C). The analysis revealed that the viscosity kept increasing with increase in concentration of CaCl₂ from 10% to 20%. However, the viscosity sees a drop when the concentration of CaCl₂ solution was raised to 30%. At a fixed shear rate of 85 s⁻¹ and under different temperature *i.e.*, ambient temperature, 40 and 90°C, C₁₈AMP3SB with 10% CaCl₂ solution exhibited viscosities between 7.5 cPs and 33.55 cPs. Likewise, under similar experimental conditions except changing the concentration of CaCl₂ solution to 20%, the viscosity ranged between 7.78 cPs and 102 cPs and for 30% CaCl₂ solution; it was observed to be between 5.75 cPs and 24.09 cPs (Fig. 2).

Similarly, the viscosity behavior of neat zwitterionic gemini surfactants (1-3) were also studied in different



Fig 8 Gel breaking properties using diesel oil in CaCl₂-20% at 90°C (a) $C_{18}AMP3SB$ (b) $C_{18}AMP3SB + 1$ (c) $C_{18}AMP3SB + 2$ and (d) $C_{18}AMP3SB + 3$

concentrations of CaCl₂ solutions (10–30%w/w) at varied temperatures (RT-90°C) with varying shear rates (1–85 s⁻¹). The results suggested that the none of gemini surfactants (1–3) alone exhibit any appreciable viscosity change under these experimental conditions. However, the mixture of surfactants (1–3) each in combination with C₁₈AMP3SB (1:1) displayed significant upsurge in the viscosity. The results suggested a trend in decrease in viscosity with increasing shear rate, which suggested that the solutions containing the mixture of C₁₈AMP3SB and gemini surfactants are non-Newtonian fluids. In other words, the viscosity of the mixture of C₁₈AMP3SB and gemini surfactants decreases with increase in shear rate (Figs. 1–4). Moreover, the mixture of surfactants (1–3) each in combination with C₁₈AMP3SB in CaCl₂ solutions demonstrated better shear rate resistance, which suggested that the calcium ions encourage the formation of wormlike micelles (rod-shaped micelles). For example, the mixture of surfactant **1** with **C**₁₈**AMP3SB** (1:1) showed up to 4–5 folds enhancement in viscosity. At a fixed shear rate of 85 s⁻¹ and under different temperature *i.e.*, ambient temperature, 40 and 90°C, the mixture in 10% CaCl₂ solution displayed viscosity ranging between 5.06 and 7.07 cPs. Likewise, in 20% CaCl₂ solution the viscosity varied from 3.31 to 14.6 cPs and for 30% CaCl₂ solution it was observed to between 6.2 and 9.77 cPs (Fig. 3).

Likewise, the mixture of surfactant **2** and $C_{18}AMP3SB$ (1:1 wt/wt) at a fixed shear rate of 85 s⁻¹ and under different temperature *i.e.*, ambient temperature, 40 and 90°C, with 10% CaCl₂ solution showed viscosity in the range

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between 3.61 and 13.13 cPs; for 20% CaCl₂ solution the viscosity varied from 5.05 to 36.33 cPs and for 30% CaCl₂ solution 5.44 to 30.06 cPs (Fig. 4).

Moreover, at a fixed shear rate of 85 s⁻¹ and under different temperature *i.e.*, ambient temperature, 40 and 90°C, the mixture of surfactant **3** and **C**₁₈**AMP3SB** (1:1 wt/wt) with 10% CaCl₂ solution showed viscosity in the range between 4.09 and 14.72 cPs; for 20% CaCl₂ solution viscosity varied from 3.35 to 37.62 cPs and for 30% CaCl₂ solution, 2.82 to 35.22 cPs (Fig. 5).

Effect of Temperature on the Viscosity

As a stimulation fluid is pumped downhole it sees rise in the temperature. The behavior of the fluid as a function of temperature is an important parameter. Thus, it is pertinent to investigate the effect of temperatures on the viscosity build up for viscoelastic surfactants. The temperature dependence of the new VES molecules was investigated over a temperature range of ambient to 90°C. It is assumed that the rise in the temperature leads to increase in the thermal motion of the molecules, which causes the network microstructure of viscoelastic surfactants to transform into single wormlike micelles (Mao et al., 2018). However, the presence of excessive Ca^{+2} ions on the surface of small micelles inhibits the recovery of wormlike micelles and network structure. But, higher temperature can contribute toward desorption of excessive Ca⁺² ions and thus can promote recovery of wormlike micelles and network structure. The mechanism for heat response has been well studied by Davies et al. on CTAB and salicylic acid system (Davies et al., 2006). Another important effect of heating was that the intense motion of hydrophobic chains promoted the twining of surfactant for stronger network building (Mao et al., 2018). Therefore, the neat C₁₈AMP3SB and the mixtures of C₁₈AMP3SB with surfactants (1-3) in varied concentration of CaCl₂ solutions (10-30%w/w) exhibited increase in the viscosity with increase in temperature from ambient to 90°C (Fig. 6).

The stability of the viscosity of $C_{18}AMP3SB$ alone and as a mixture in combination with surfactants (1–3) in CaCl₂ solutions (20%w/w) under shear rate of 85 s⁻¹ at 90°C was tested for one hour the mixtures of $C_{18}AMP3SB$ with surfactants (1–3) in CaCl₂ solutions (20%w/w) under shear rate of 85 s⁻¹ at 90°C was tested for one hour. The results showed that there was no appreciable change in viscosity with time and the viscosity remains stable throughout the experiment (Fig. 7).

Gel Breaking Properties

It is hypothesized that the viscosified VES gel will break once it encounters the produced hydrocarbon. It is important that the VES gel viscosity gets reduced for better cleanup during hydrocarbon production. Any remaining high viscosity gel will lead to damaging the reservoir by blocking the hydrocarbon. To confirm the hypothesis, gel breaking properties of neat surfactants and their mixtures were studied by mixing them with diesel, from 1.53% to 15.66%, in the presence of 20% CaCl₂ solution. These results suggested that the viscosity of C18AMP3SB dropped from maximum (102 cPs) to minimum (7.2 cPs) upon addition of 5% diesel at 90°C. Moreover, any further addition of diesel led to enhance the viscosity again (Fig. 8a). Likewise, mixture of surfactant 1 and C18AMP3SB (1:1 w/w) also displayed decline in the apparent viscosity up to 11.02% followed by an increase upon further increase in the diesel concentrations (Fig. 8b). Similarly, the gel breaking of mixture of surfactant 2 and C18AMP3SB (1:1 w/w) was decreased from 36.33 to 7.5 cPs with rise in concentration of diesel up to 5.83%. However, the viscosity then tends to increase with rise in any further diesel concentration (Fig. 8c). Finally, a considerable change in viscosity was also seen in the case of surfactant 3 and C₁₈AMP3SB (1:1 w/w). The gel breaking occurred with 11.02% of diesel addition, which was then started increasing with any further increase in diesel concentration (Fig. 8d).

Conclusions

Three new zwitterionic gemini surfactants (1-3) and a previously known amidosulfobutaine (C18AMP3SB) were synthesized from commercially available fatty acids using a straight-forward synthesis. The chemical structures of these surfactants were characterized by spectroscopic methods including ¹H and ¹³C NMR, and IR spectroscopy. Moreover, these surfactants exhibited excellent thermal stability, determined by TGA. At varied temperature and different shear rates, the viscosity of mixture of zwitterionic gemini surfactants (1-3) with amidosulfobutaine (C₁₈AMP3SB) showed promising buildup of viscosity. The individual C18AMP3SB surfactant and its combinations with zwitterionic gemini surfactants (1-3) performed best in the presence of 20% CaCl₂ solution at 90°C showing the apparent viscosity of 102, 14.6, 36.33, 37.62 cPs, respectively. The properties of these surfactants warrant their potential for a possible use in various oilfield applications.

Conflict of Interest The authors declare that they have no conflict of interest.

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