The Role of Nanoparticle-Gemini Surfactant to Improve the Flowability of the Malaysian Crude Oil

Shamala Devi VijayaKumar, Junaidi Zakaria, and Norida Ridzuan

Abstract Wax deposition on the inner walls of transportation pipelines and production equipment of Malaysian crude oil had been identified as one of the main encounters in the crude oil industry which leads to serious problem in crude oil flow assurance. In this research, the performance of a Gemini surfactant, nanoparticle and their blends are assessed to study their impacts on the viscosity of crude oil using rheometer. Silicon dioxide (SiO_2) (200–600 ppm) along with Gemini surfactant (ethoxylated-2,5,8,11-tetramethyl-6-dodecyn-5,8-dio) (200–1000 ppm) at different temperature (10–30 °C) were studied to discover the effect on viscosity. From the results, the most efficient viscosity reducing concentration of Gemini surfactant, nanofluid and nanoparticle-Gemini surfactant was found at the concentration of 400 ppm, 300 ppm and 200 ppm, respectively. At 30 °C and 80 rpm, the viscosity of the crude oil is reduced from 3.75 to 3.5 cP compared to the blank crude oil. Addition of SiO_2 nanoparticle to Gemini surfactant, resulted in reduction of viscosity of the crude oil from 3.75 to 1.5 cP. At temperature 10 °C, Gemini surfactant reduced the viscosity of crude oil from 51.95 to 4.5 cP, while the addition of SiO_2 nanoparticle only reduced the viscosity from 51.95 to 3.75 cP. As a conclusion, the addition of nanoparticle-Gemini blend shows the significant result at low temperature where it shows the best reduction of crude oil viscosity.

Keywords Nanoparticle · Shear rate · Temperature · Viscosity · Wax inhibitor

1 Introduction

Crude oil industry is one of the major industries in Malaysia where the continuity of production and supply is crucial in order to fulfill the crude oil demand. However, the most common challenge faced by the industry during the production and transportation of Malaysian crude oil is wax deposition and this poses a large problem

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when it deposits inside the pipelines. Crude oil is transported and processed at low temperatures which causes precipitation of wax particles that leads to pressure drop in the production pipeline and processing equipment which results in plugging [1–3]. The buildup of wax in crude oil pipeline and process equipment is a main concern in the petroleum industry. The process of cleaning wax buildup requires shutdown and therefore, the maintenance cost is extremely expensive.

Wax deposition has been a critical operational challenge and imposes major flow assurance problem in the oil industries including the offshore and onshore oil field around the world for many years. Wax precipitation is caused by a few factors such as crude oil composition, viscosity, temperature gradient, production time and shear stress. However, viscosity is recognized as an extremely significant cause of wax deposition rate and prompts wax precipitation and thus need to be reduced in order to make the transportation of crude oil easier [4]. As the bulk oil temperature decreases below its wax appearance temperature [5], wax particles start to precipitate and forms high yield wax gel, that eventually covers the pipeline. The continuation of this process results in gelation where the wax particles aggregate and precipitate in oil cluster as the temperature and pressure changes [3, 6]. This condition leads to poor fluidity of crude oil due to the gelation of wax layer.

Current solutions to overcome wax deposition issue are mainly heating techniques and mechanical removal. However, these methods are not economical as heating requires the use of steam and frequent replacement of electrical heaters while mechanical removal causes temporary shutdown of production [7]. Past researches showed chemical wax inhibitors are commonly used to overcome wax deposition in crude oil as they are more efficient and economical. Heretofore, several chemicals have been used as to improve flowability of crude oil such as, N,N-Dimethyl-N-[2-hydroxy-3-sulfo-propyl]-N′-phenyloctadecanoyl-1,3-diaminopropane [8], (3-(2-methoxyethoxy)propyl-methyl-bis (trimethylsilyloxy) silane) with silicon dioxide [9], Polycarboxilate/poly acrylate/poly vinyl acetate [10], Poly acrylate ester copolymer [11], Ethylene vinyl acetate-co-diethanolamine [12], N,N-bis(dimethyl alkyl)-a, ω-alkanediammoniumdibromide with zinc oxide [15] and Poly (hexyl oleate-co-hexadecyl maleamide-co-n-alkyl oleate) [13]. The advantage of wax inhibitor addition to the crude oil sample is that the deposition can be mitigated without stopping production. The addition of ethylene-co-vinyl acetate and Poly maleic anhydride-alt-1-octadecene with sodium cloisite on crude oil showed that nanoparticle alone reduced the crude oil viscosity approximately 92.5%, EVA and MA reduced up to 88% and 86.4%, while EVA and MA with nanoparticle reduced to 94% and 89.2% respectively [5].

Investigation of interfacial tensions of fatty alcohol polyoxyethanol carboxylate (C_nEO_mC) which is an anionic-nonionic surfactant on crude oil showed that mixed solution of $C_{14}EO_3C$and $C_{14}EO_7C$ with mass fraction ratio of 1:1 can reduce the interfacial tension of crude oil to ultralow values [16]. This can be achieved by adjusting the hydrophilic-lipophilic balance and proportions compatibility. In a study of enhanced oil recovery, N,N′-bis((dimethyltetradecyl)-1,6-hex-anediammonium bromide) Gemini surfactant, partially hydrolyzed poly-acrylamide polymer and/or silica nanoparticle were characterized in terms of rheology and surface tension [17].

The results found that nanoemulsions generally showed shear-thinning behavior that enables injectivity at high shear rates and for improving recovery efficacy at low shear rates. Nanoparticles efficiently adsorbs onto the nanoemulsion surface, decreasing the surface energy. This proves that SiO_2 addition upsurges the adsorption of emulsifier molecules at the interface [17].

Research on plant seed oil also had been done to study their effect on wax deposition where Jatropha seed oils and castor seed oils (CSO) are used and the result showed that the blend of CSO with 40% JSO reduced the wax deposition and gave best impacts on the pour point with paraffin inhibition efficiency of 79.1% [18]. There are also researches being done on the use of nanotechnology in overcoming wax deposition problem. As such, polyacrylamide (PAM) with varying concentrations of nanoclay for an optimum viscous solution was investigated and the findings revealed that a specific range of nanoclay content had encouraging effect on PAM viscosity, aluminium and silicon containing nanofluids caused the highest and lowest viscosity at all temperature, respectively, and the increase in viscosity was noticeable when silicon oxide nanoparticle concentration was increased [19]. However, the effects of nanoparticles, wax inhibitor and their blends on the viscosity of Malaysian crude oil is uncertain, and there are limited researches on this field. This research is aimed to evaluate the effect of Gemini surfactant (ethoxylated-2,5,8,11-tetramethyl-6-dodecyn-5,8-dio), nanoparticle silicon dioxide (SiO_2) and their blend on the viscosity of crude oil at various temperature and shear rate.

2 Methodology

2.1 Materials

Raw crude oil was supplied by PETRONAS Penapisan Terengganu Sdn. Bhd. The crude oil wax appearance temperature (WAT) is 28 °C [5]. Gemini surfactant 2,5,8,11-tetramethyl-6-dodecyn-5,8-diol ethoxylate was used as wax inhibitor which was supplied by Evonik Corporation. The nanoparticle used was silicon dioxide (SiO_2) nanoparticle with a particle size of 20 nm purchased from Nanou Nanotechnology.

2.2 Preparation of Gemini Surfactant

To prepare 250 mL Gemini surfactant solution with 1000 ppm concentration, 0.25 mL of Gemini with 1,000,000 ppm concentration was diluted into cyclohexane in 250 mL volumetric flask. The solution was stirred for 1 h at 25 °C and 700 rpm to get a homogenous solution. 1000 ppm Gemini solution was then diluted using cyclohexane into 800, 600, 400 and 200 ppm concentrations.

2.3 Preparation of Nanoparticles Fluid (Nanofluid)

To prepare 250 mL of SiO_2 solution with 5000 ppm concentration, 1.25 g of SiO_2 powder was mixed with 250 mL of cyclohexane and stirred for 2 h at 60 °C and 700 rpm followed by ultrasonication treatment for a time period of 30 min at 25 °C. SiO_2 solutions of 5000 ppm was then diluted using cyclohexane into 200, 300, 400, 500 and 600 ppm concentrations.

2.4 Preparation of Nanoparticle and Gemini Surfactant Blends

To prepare nanoparticle Gemini surfactants blend, the ratio of Gemini surfactant solution to nanofluid used was 3:1. 3 wt% of Gemini surfactants was mixed with 1 wt% of nanofluid. The total volume for the blends was 10 mL. The mixture was continuously stirred for 1 h at 50 °C and 700 rpm to get a homogenous solution.

2.5 Viscosity Analysis

The Brookfield Viscometer model DV-III was used to measure the crude oil viscosity at various shear rates (80–200 rpm). The viscosity measurement was conducted using nanofluid and Gemini surfactant solution with and without the addition of nanofluid. The samples were heated above wax appearance temperature before starting experiment to completely dissolve wax crystals. The temperature varied within the range of 10–30 °C.

3 Results and Discussion

3.1 Effect of Temperature on the Viscosity of Blank Crude Oil

Figure 1 demonstrates the blank crude oil viscosity against temperature at a fixed shear rate of 80 rpm. The viscosity of crude oil is lower at the higher temperature which was 3.75 cP. From the figure, when the temperature approaches WAT, the viscosity starts to increase and below WAT, the viscosity becomes as high as 51.95 cP at 10°C, where wax begins to form, causing poor fluidity.

Below the WAT, wax particle aggregates initiate the nucleation process and forms crystals. The crystals grow in size with the increasing accumulation of atoms [20] and leads to wax precipitation. Wax precipitation occurs when dissolved wax molecules in crude oil solidify with respect to the function of temperature and enthalpy of

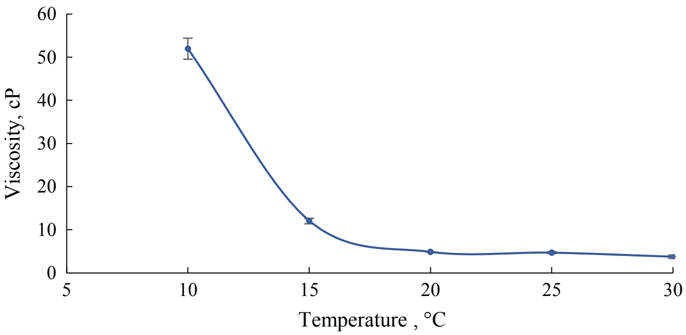

Fig. 1 Viscosity of blank crude oil at different temperatures

crystallization [21]. Thus, the wax particles begin to crystallize and causes rise in blank crude oil viscosity.

3.2 Effect of Addition of Nanoparticles on the Viscosity of Crude Oil

The addition of SiO_2 nanoparticle had significant effect on the crude oil viscosity reduction, specifically at lower temperature. Figure 2 shows the viscosity of crude oil at different concentrations of nanofluid against shear rate at different temperature. At 30 °C and 80 rpm, the lowest crude oil viscosity was obtained at 3.0 cP while the highest was 7.5 cP at 20 °C and 100 rpm. Below WAT, the viscosity of crude oil decreased with incorporation of silicon dioxide but there was not much effect as the temperature approached WAT. As shown in Fig. 2, at a shear rate of 80 rpm, the lowest viscosity for all nanofluid concentration was obtained. Apart from temperature, shear rate also influenced the viscosity of crude oil. Above 100 rpm, the viscosity decreased as the shear rate increased. However, at the shear rate of 100 rpm, the viscosity of crude oil increased slightly. This happens due to the shear thickening fluid behavior resulting from a very viscous liquid. At higher shear rate, the non-Newtonian behavior promotes wax formation in crude oil through crystallization process [22]. This leads to wax crystal aggregation resulting in higher viscosity reading. The concentration of nanofluid influences the effectiveness of viscosity reduction. From Fig. 3, the most efficient concentration of nanofluid to generate the lowest viscous crude oil is found at 300 ppm and 30 °C. While at 10 °C, the viscosity of the crude was drastically reduced from 51.95 to 5.25 cP.

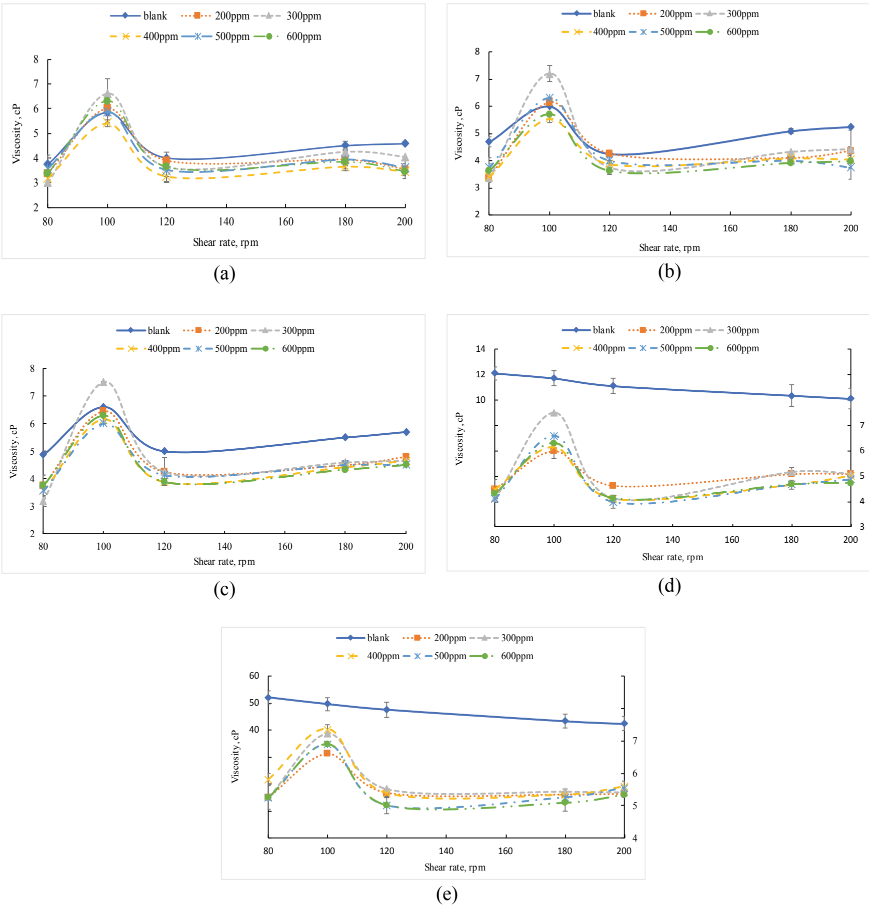

Fig. 2 The effect of viscosity at different range of shear rate and nanofluids concentrations at various temperature; **a** 30 °C, **b** 25 °C, **c** 20 °C, **d** 15 °C, **e** 10 °C

3.3 Effect of Gemini Surfactant with and Without the Incorporation of Nanoparticle on the Viscosity of Crude Oil

The viscosity of crude oil was reduced upon the addition of Gemini surfactant and additional reduction was observed with the addition of nanofluid. Addition of SiO_2 showed significant viscosity reduction and it works well with Gemini surfactant. Figures 4 and 6 demonstrates the impact on crude oil viscosity at different Gemini surfactant concentrations and at different concentration of nanofluid with the most efficient viscosity reducing concentration of wax inhibitor which is 400 ppm respectively. Gemini surfactant as wax inhibitor in this research gave significant effect as the

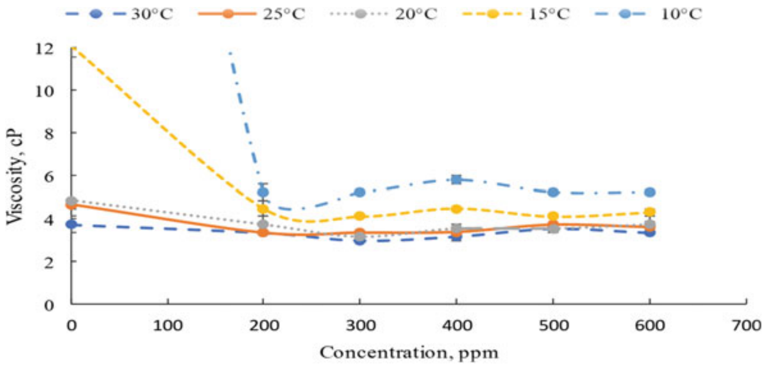

Fig. 3 The effect of different nanofluid concentrations on the viscosity of crude oil at various temperature and at shear rate of 80 rpm

addition of wax inhibitor into crude oil reduced the viscosity at temperature as low as 10 °C, from 51.95 to 4.5 cP as shown in Fig. 4. The crude oil viscosity decreases when temperature rises from 10 to 30 °C. When the wax molecules start to drop below WAT, the crude oil viscosity started to increase, as wax started to form. Wax inhibitor adsorbs onto wax crystals, forming wax crystal lattice assembly in the crude oil that reduces the growing crystals' morphology and interrupts the development of a three-dimensional crystal [6]. A wax dispersant absorbs itself onto the surface of wax to prevent crystal aggregation by preventing the crystal nucleation between crystal surfaces [21].

From Fig. 5, the most efficient viscosity reducing concentration of Gemini surfactant is 400 ppm. The graphs validate that the crude oil viscosity is not impacted by Gemini surfactant concentration as higher concentration showed higher viscosity reading as compared to wax inhibitor of 400 ppm. This can be due to precipitation of higher concentration wax inhibitor [5].

Gemini surfactants consists of two hydrophilic head groups with two hydrophobic tails linked by a spacer at or near the head groups [23]. The spacer can pose rigidity or flexibility that determines their hydrophobicity or hydrophilicity. It is a vital part of Gemini surfactant that regulates the surface adsorption, and the self-assembly aggregation. Some of the ultimate qualities of surfactants is their ability to adsorb at interfaces, high surface activity, low critical micelle concentration (CMC) values and good synergy [14]. A wax dispersants adsorbs onto wax crystals and forms a wax crystal lattice assembly in the crude oil which delays the formation of wax crystals [6]. Figure 6 shows that there is a further reduction in viscosity after the addition of nanofluid together with wax inhibitor. At temperature of 30 °C, above WAT, the viscosity reduced from 3.75 to 1.5 cP after the addition of wax inhibitor and SiO_2 with a load ratio of 3:1, noting the lowest viscosity at nanoparticle concentration of 200 ppm as shown in Fig. 7. Wax inhibitor with most efficient viscosity reducing nanoparticle concentration reduced the viscosity of crude oil from 51.95 to 3.75 cP at 10 °C.

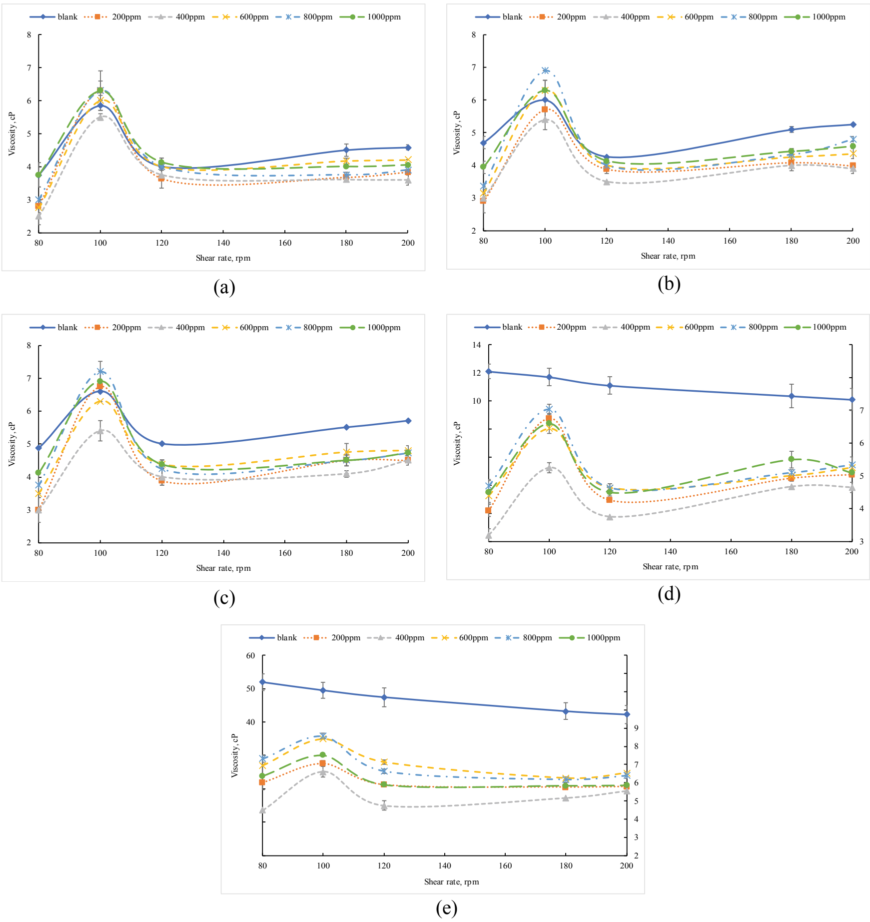

Fig. 4 The effect of viscosity at different range of shear rate and wax inhibitor concentrations at various temperature; **a** 30 °C, **b** 25 °C, **c** 20 °C, **d** 15 °C, **e** 10 °C

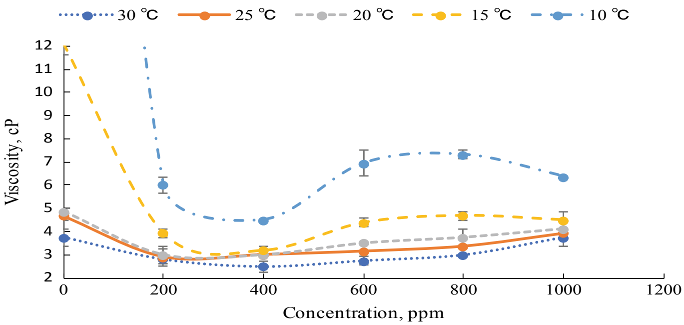

Fig. 5 The effect of different Gemini surfactant concentrations on the viscosity of crude oil at varying temperature and at shear rate of 80 rpm

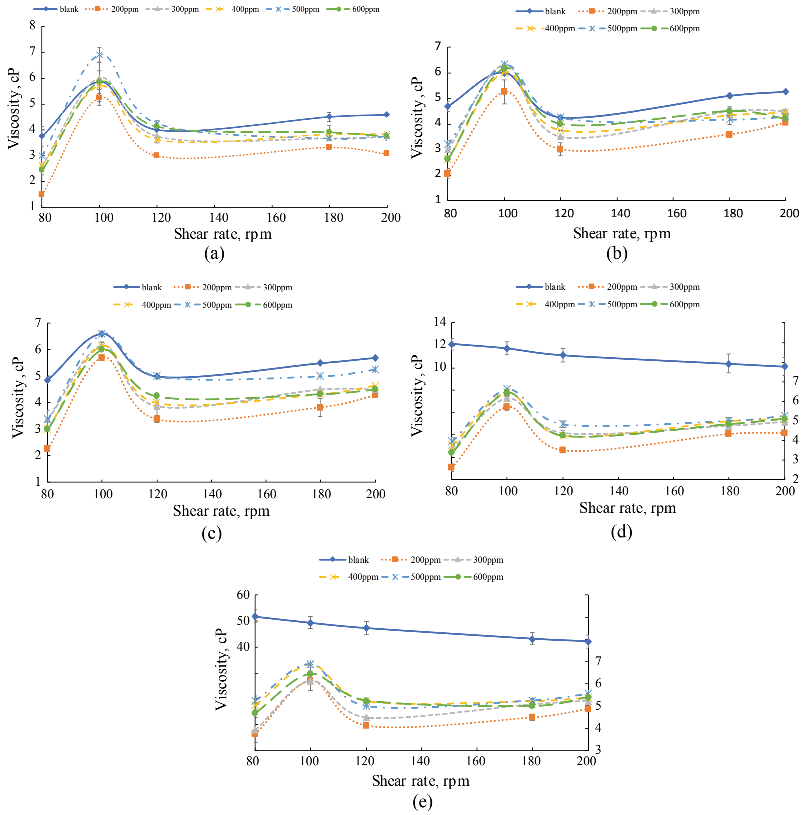

Fig. 6 The effect of viscosity at different range of shear rate and different concentrations of nanofluid with wax inhibitor 400 ppm at various temperature; **a** 30 °C, **b** 25 °C, **c** 20 °C, **d** 15 °C, **e** 10 °C

4 Conclusion

The addition of Gemini surfactant and silicon dioxide nanoparticle enhances the continuity flow of crude oil through viscosity reduction. The performance of the Gemini surfactant, however, depends on the concentration and shear rate, where the most efficient viscosity reducing concentration and shear rate were found to be 400 and 80 rpm. The addition of silicon dioxide nanoparticle and Gemini surfactant together gave the best effect of viscosity reduction which is 1.5 cP at the ratio of 3:1 to Gemini-nanoparticle. Nanotechnology can contribute to more effective, cheaper, and more environmentally friendly solutions than current solutions. Nanoparticle alone gave a significant reduction in viscosity.

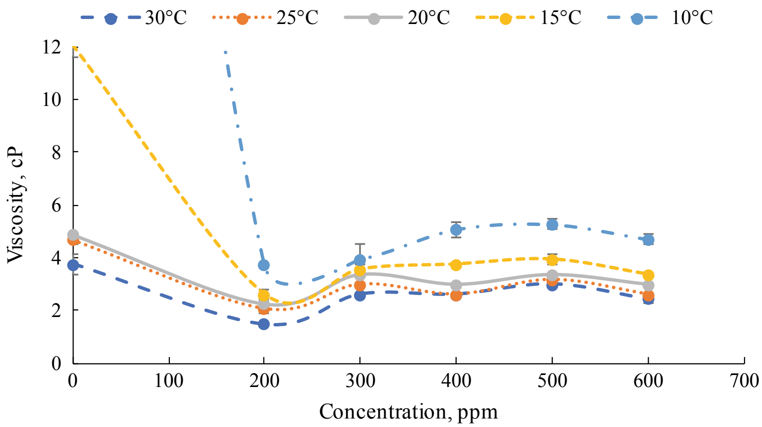

Fig. 7 The effect of different nanofluid concentrations with wax inhibitor 400 ppm on the viscosity of crude oil at varying temperature and at shear rate of 80 rpm

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