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One-pot Synthesis and Static Bulk Foam Studies of C₁₈-conjugated Zwitterionic Surfactant

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Abstract. This study reports a one-pot-synthesis of C₁₈-conjugated zwitterionic surfactant, linolyel dimethyl amidopropyl betaine (Lino-DAB) for application in oil and gas industry. The synthesis proceeded with the direct thermo-condensation of N,N-dimethyl-1,3-propanediamine with C₁₈-polyunsaturated omega-6 fatty acid (linoleic acid) and subsequent treatment with sodium chloroacetate. The structure of the (Lino-DAB) products (19 g) was identified by ¹H-NMR and FTIR experiments and by comparing with the other long chain zwitterion surfactants from the literature. The static bulk foam tests in the absence and presence of crude oil under range of reservoir conditions (0 - 3.5 % salinity and 25 – 90 °C temperature) were conducted, the results indicated that the high salinity and presence of crude oil were detrimental to the foamability of the Lino-DAB (0.2 %) at ambient condition (25 °C), but the foamability were significantly improved at the higher temperature (60 – 90 °C). Similarly, the Lino-DAB exhibits viscoelastic properties in brine solutions and has the ability to retain its viscosity by 10% at 90°C. Thus, this study demonstrates that Lino-DAB surfactant could have a potential application to enhance oil recovery particularly in foam assisted flooding.

Keywords: Surfactant, Foam, Enhanced oil recovery, amphoteric

1. Introduction

Enhanced oil recovery surfactants (EOR-surfactants), commonly known as surface active agents or foaming agents are compounds having hydrophilic head and hydrophobic chain tail capable of orienting at the medium interface and reduce the interfacial/surface tension by thinning effect [1-3]. The nature of the hydrophilic head group classifies the EOR-surfactants into anionic (sodium dodecyl benzene sulfonate), non-ionic (polyoxyethylene alcohol), cationic (trimethyldodecylammonium chloride) and zwitterion (dodecyl betaine) [4]. In the tertiary enhanced oil recovery (EOR), the EOR-surfactants are employed mainly to lower the interfacial tension of the oil/water system or to achieve a gas mobility control in the foam assisted flooding EOR [5, 6]. Foam flooding technique is the emerging EOR method to address the trending viscous fingering and gas gravity segregation [7]. Various EOR-surfactants have been successfully employed, but their foamability showed sensitivity towards reservoir conditions which led to poor performance in the oil field [8, 9]. It is important for the EOR-surfactants to be economically available and resist the effects of reservoir brine, temperature,



pressure and crude oil. However, the zwitterionic surfactants, which have both the cationic and anionic on the hydrophilic head offer greater market demand within the oil industry because of the improved properties compared with other classical surfactants [10]. Consequently, more and more zwitterionic surfactants with viscoelastic properties have been synthesized through many processes [10, 11]. The present study is aimed at synthesizing a new class of zwitterion surfactant through a one-step synthesis approach. Furthermore, static bulk tests were investigated at various conditions typically found in the oil reservoirs to assess the foamability of the surfactant.

2. Material and Methods

The chemicals, N,N-dimethylpropylidiamine, sodium chloroacetate, sodium hydroxide and potassium hydroxide were of analytical grades purchased from the Sigma Aldrich company. The double distilled water was used for all the preparations.

2.1. One-step synthesis of zwitterionic surfactants

Exactly 20 mL of the linoleic acid was transferred into the two neck flask and heated gently between 80 – 90 °C for 15 min. Thereafter, few drops of N,N-dimethylpropylidiamine was slowly added to the reaction flask drop by drop and the temperature was raised gradually to 180 °C and refluxed under nitrogen for 5 hrs (Figure 1a). At this stage, elimination of water molecule occurred due to the intermolecular condensation of dimethylpropandiamine with the linoleic acid (Figure 2) and the reaction was monitored by Fourier transform infrared spectroscopy (FTIR). Subsequently, sodium chloroacetate (3.5 g), sodium hydroxide (9 g) and potassium hydroxide (5 mL) were then added and the reaction temperature was reduced to 80 °C and heated for 17 hrs until a solid yellowish/amber paste was formed (Figure 1b). To monitor the completion of the reaction, at an interval of time, small solid paste product was dissolved in a distilled water until a clear and homogeneous solution was obtained and finally the product structure (Figure 1c) was confirmed by the ¹H-NMR and FTIR spectroscopy.

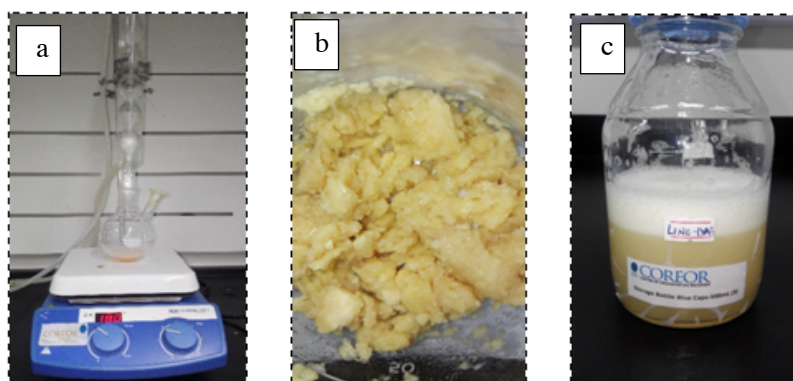


Figure 1. (a) Synthesis reaction set-up, (b) Lino-DAB solid paste after the reaction, (c) Lino-DAB Stock.

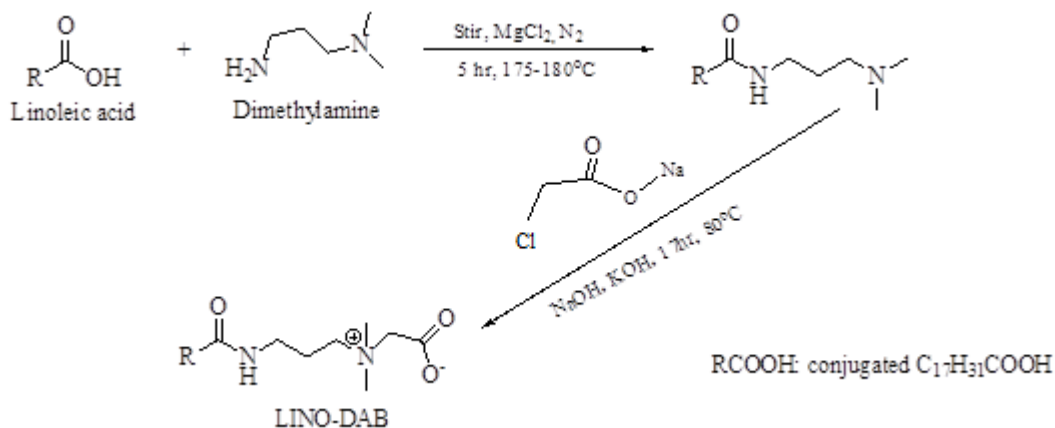


Figure 2. Synthesis of Lino-DAB surfactant.

2.2. Characterization

Fourier transform infrared spectroscopy (FTIR) of the material was recorded using PerkinElmer Spectrum ISO AKX1300573 Nexus FTIR. ¹H-NMR spectra was recorded in deuterated water (D₂O) at room temperature using a Bruker AvanceIII 500 MHz with tetramethylsilane (TMS) as an internal standard.

2.2.1. Salinity effect on the foamability in the absence and presence of oil

Exactly, 50 mL of the Lino-DAB (0.2 %) solutions were prepared in different NaCl brine concentrations (from 0 - 3.5 %), respectively. These solutions were separately transferred into a laboratory blender to generate foams within 30 s at 25 and 90 °C, respectively. These experiments were performed in triplicates to obtain the mean maximum foam volumes in the graduated cylinder. The same experiments were carried out in the presence of a crude oil at 95:5 % surfactant: oil ratio.

2.2.2. Temperature effect on the foamability in the absence and presence of oil

About 50 mL of the Lino-DAB (0.2%) in a fixed 3.5 % brine was heated at 25, 60 and 90 °C, respectively, and foams were generated using air in the absence and presence of crude oil (95:5 % surfactant: oil ratio). These experiments were performed in triplicates to obtain the mean foam volume.

2.2.3. Salinity effect on the viscosity of surfactant at ambient condition

The dynamic viscosity of the Lino-DAB (0.2 %) was performed according to ASTM D445 using modular compact rheometre (MCR 300). The viscosity of the surfactant in different brine regime (0 - 3.5 %) were analyzed at 25 °C and constant shear rate of 50 s⁻¹. Exactly, 10 viscosity data points were recorded for each and from which the mean viscosity was computed. The plot of viscosity against salinity was plotted.

2.2.4. Temperature effect on the viscosity of surfactant

The effect of temperature on the viscosity of the Lino-DAB surfactant (0.2 %) was also investigated. The viscosity measurement was performed at a fixed salinity concentration (3.5 %). The temperature was ramped from 25 to 90 °C at constant shear rate of 50 s⁻¹. Exactly, 30 viscosity data points from 25 – 90 °C were used to plot the correlation between the viscosity and temperature.

3. Result and Discussion

3.1. Characterization

From Figure 3, it can be seen that due to the condensation reaction between the linoleic acid (RCOOH) and diamine R(NH)₂, elimination of water molecule had occurred leading to the formation of an intermediate secondary amine (RNHR) product which was confirmed by FTIR as shown in

Figure 3, this secondary amine (N-H) was confirmed due to the stretching vibrations around 3355.75 cm^{-1} , bending at 1645.06 cm^{-1} and wagging at 723 cm^{-1} . The intensity which was due to the C=O stretching vibration was also seen at 1742.80 cm^{-1} while the C-N vibration was absorbed at 1159.47 cm^{-1} . Similarly, the absorptions at 2914.33 and 2852.67 cm^{-1} was assigned to C-H, CH₂ and CH₃ groups. After, the reaction had proceeded in the presence of chloroacetate, a blue shift was observed in the absorption frequencies and the the intensities due to C=O and N-H further confirms the formation of the Lino-DAB product. The assignments of these absorption frequencies were in accordance to the DAB derivatives surfactant synthesized from other class of fatty acids, like erucic, oleic and gondoic acids [1, 10, 12] and also from the scientific books of the FTIR absorption frequency correlation table.

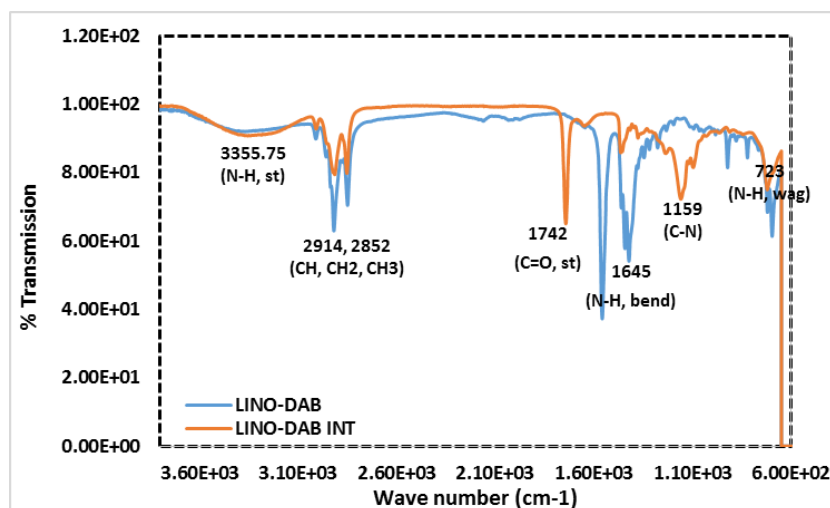


Figure 3. The FTIR spectra of the Lino-DAB during and after the reaction.

The FTIR of the Lino-DAB product was confirmed by the ¹H-NMR spectroscopy experiment (Figure 4) (500 MHz, D₂O) δ ppm; 0.82 (3H, t, alkyl -CH₃, H-1), 1.22 (14H, m, alkyl chain -CH₂, H-2), 1.44 (2H, m, β-CH₂, to C=O, H-3), 1.93 (4H, m, -CH₂, H-4), 2.05 (2H, t, α-CH₂ to C=O, H-5), 2.67 (2H, t, -CH₂, H-6), 3.44 (4H, m, -CH₂, H-7), 3.54 (6H, m, N-CH₃, H-8), 4.75 (2H, s, -CH₂, H-9), 5.22 (4H, m, HC, H-10) and 8.36 (1H, s, N-H, H-11).

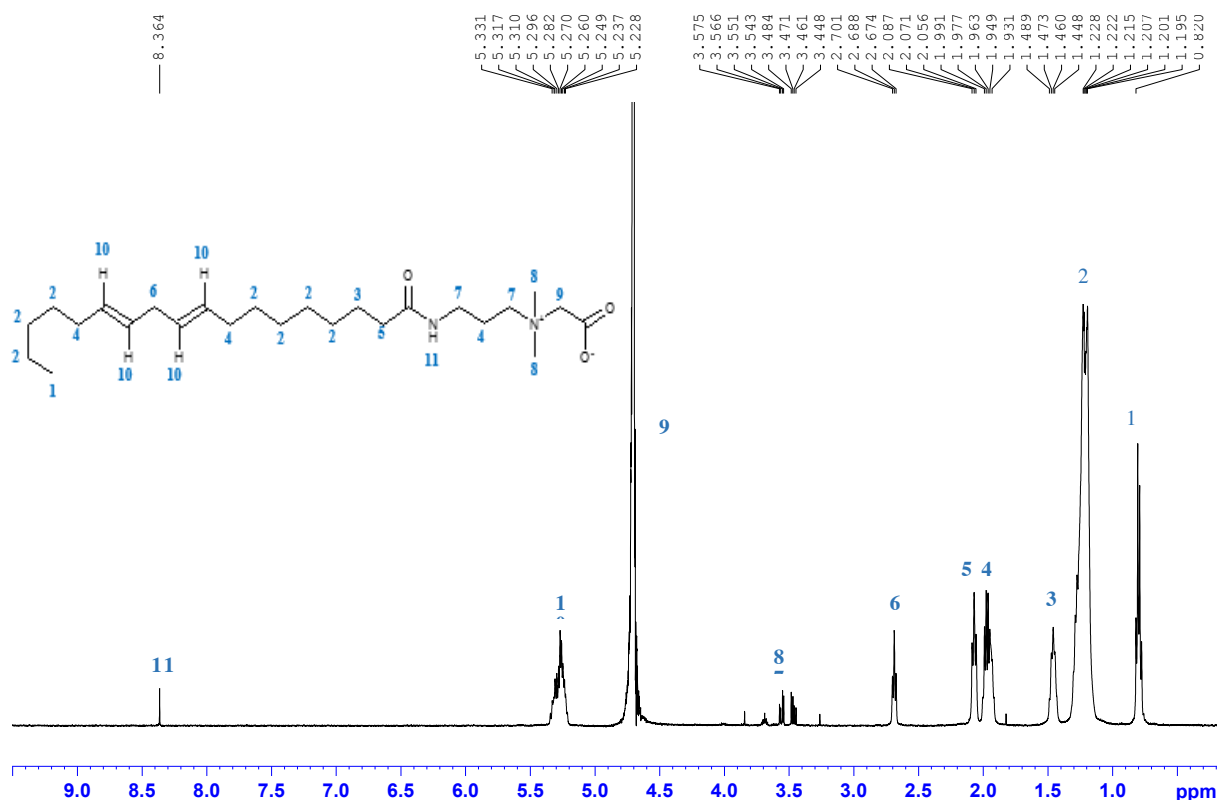


Figure 4. $^1\text{H-NMR}$ (500 Mz, D₂O) spectra of Lino-DAB.

3.2 Salinity effect in the presence and absence of crude oil at 25 and 90 °C

In the EOR-foam assisted flooding, water (brine) and gas are alternatively injected to generate foam in order to sweep the oil from the reservoir [13]. The water used in this aspect is a mixture of surfactant and brine in different concentration ratios. The generated foam in the porous body is believed to be affected by various reservoir conditions (salinity, temperature and crude oil), therefore, it is crucial to investigate the effect of salinity, temperature and the crude oil on the foamability of surfactants. In this study, the effect of salinity (0 - 3.5 %) in the absence and presence of the crude oil at 25 and 90 °C are presented in Figure 5. From the Figure 5a, it can be seen that at ambient condition (25 °C), the salinity is detrimental to the foamability of the Lino-DAB both in the presence and absence of the crude oil, respectively. The result shows that by increasing the salinity, the foamability reduced significantly in each case. The decrease in the foamability was the result of the viscosity increase of the foaming surfactant, making it difficult to generate foam at higher salinity. Evidence of this viscosity increase due to the salinity was discussed in the viscosity section. However, the salinity effect was more detrimental to the foamability in the presence of the crude oil because no further foam volumes were seen from the 2 - 3.5 % salinity conditions, unlike in the absence of crude oil. It can also be observed that, apart from the salinity effect, presence of the crude oil also impacts additional detrimental effect on the foamability, the maximum foam volumes were higher in the oil free solutions compared with the presence of crude oil at every level of salinity.

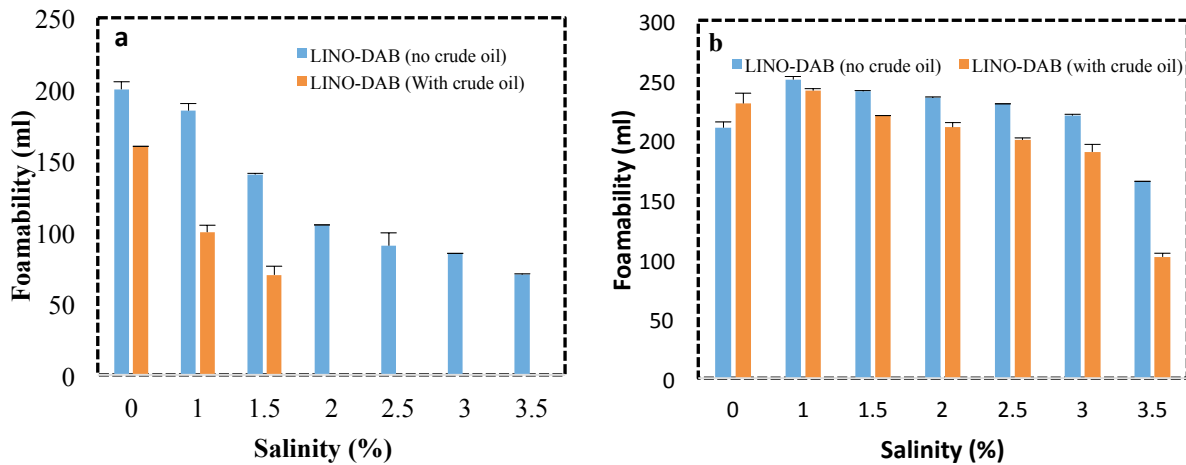


Figure 5. Influence of salinity in the absence and presence of crude oil at (a) 25°C and (b) 90°C.

Similarly, at 90 °C (Figure 5b), the foamability was noticed to increase when compared with the ambient conditions (Figure 5a). The increase of the foam volume with increasing temperature was attributed to the decrease of the viscosity [14]. However, the salinity effect was also noticed and behaved similarly at 25 °C. It can be observed that at initial salinity (1 %), the foam volume was higher than the brine free solution (0 %), this could be due to the influence of salts ions interaction with the charges of the amphoteric Lino-DAB surfactant, but the ionic strength further reduced the foam volumes at higher salinity [15].

3.3 Temperature effect in the presence and absence of crude oil at 3.5% salinity

The result of temperature effect (Figure 6) shows that the foamability increases with the increase in temperature both in the absence and presence of crude oil. This is because by increasing the temperature, the surfactant's viscosity is reduced and the foam could easily be generated [14]. Similar behavior was observed in the study of Wei, et al. [9]. This foaming behavior is typically what is required for surfactants to achieve greater effect in the reservoir, since most oil reservoirs are associated with the high salinity and temperature [16-17]. The foamability capacity was less in the presence of the crude oil even at 90 °C, this is attributed to the destructive effect of crude oil on foam bubbles [18] and low interfacial tension between the oil-gas compared with the water-gas [19].

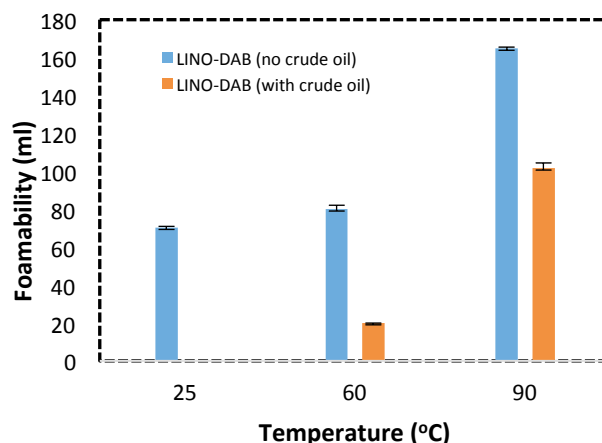


Figure 6. Influence of temperature in the absence and presence of crude oil.

3.4 Salinity effect on the viscosity

In order to correlate the salinity effect on the foamability, the Lino-DAB viscosity was investigated at salinity concentration from 0 - 3.5 %. The result is presented in Figure 7. From the result, it can be seen that there was a direct relationship between the salinity and the viscosity. Meaning that, as the

salinity is increased, so also the viscosity. This trend could support the finding of the salinity effect with respect to the foamability in the absence and presence of crude oil above. The increasing viscosity is to the advantage of the performance of this surfactant in the reservoir, reason being that, certain viscosity retention would be achieved due the reservoir temperature and apparently, the foaming capacity would be improved due the aforementioned reason in section 3.2 with regards the viscosity reduction and foamability.

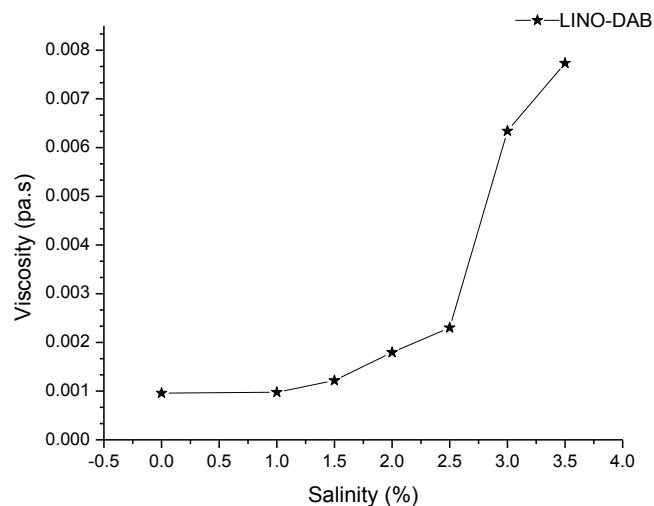


Figure 7. Effect of salinity on the viscosity.

3.5 Temperature effect on the viscosity

Figure 8 presents the result of temperature effect on the viscosity of Lino-DAB surfactant. This experiment was performed at 3.5 % salinity to investigate the extent of viscosity retention with the increasing temperature. The result demonstrated that, although, there was a sharp decrease of the viscosity when the temperature reaches around 40 °C, but the viscosity retention index was found to be about 10 % at 90 °C. Thermal stability of zwitterion surfactants is owing to the presence of carboxylate in the structure [4]. This indicates that minimum viscosity retention at higher temperature could be sufficiently enough to generate high foam volume.

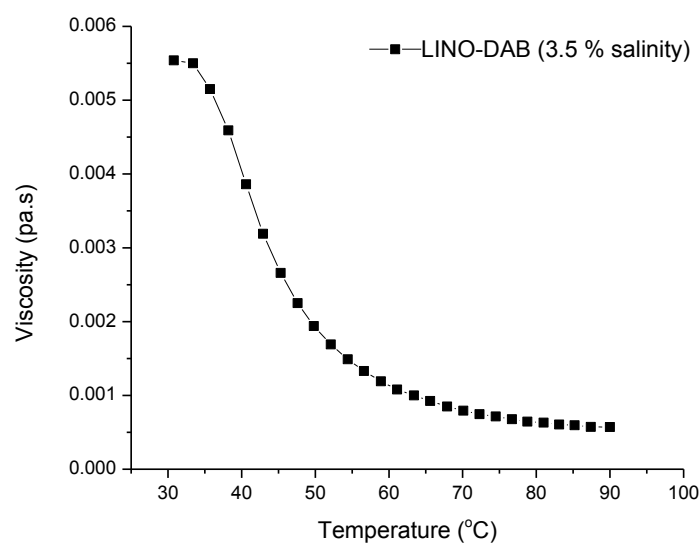


Figure 8. Influence of increasing temperature.

4. Conclusion

A conjugated EOR-surfactant (Lino-DAB) has been successfully synthesized and characterized via a one step method. The Foamability capacity of the Lino-DAB was assessed in different regimes, such as salinity, temperature and crude oil, and there was a good foamability despite effects of these conditions. The Lino-DAB surfactant being a zwitterion class of surfactant could be potentially utilized in surfactant/foam flooding EOR.

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