Effect of temperature and salt concentration on rheological behaviour of surfactin

Suleiman, SM, Abbas, AJ, Babaie, M, Akpan, EU, Yahaya, AA and Hassan, KY

<table>
<thead>
<tr>
<th>Title</th>
<th>Effect of temperature and salt concentration on rheological behaviour of surfactin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Authors</td>
<td>Suleiman, SM, Abbas, AJ, Babaie, M, Akpan, EU, Yahaya, AA and Hassan, KY</td>
</tr>
<tr>
<td>Type</td>
<td>Conference or Workshop Item</td>
</tr>
<tr>
<td>URL</td>
<td>This version is available at: <a href="http://usir.salford.ac.uk/id/eprint/51749/">http://usir.salford.ac.uk/id/eprint/51749/</a></td>
</tr>
<tr>
<td>Published Date</td>
<td>2019</td>
</tr>
</tbody>
</table>

USIR is a digital collection of the research output of the University of Salford. Where copyright permits, full text material held in the repository is made freely available online and can be read, downloaded and copied for non-commercial private study or research purposes. Please check the manuscript for any further copyright restrictions.

For more information, including our policy and submission procedure, please contact the Repository Team at: usir@salford.ac.uk.
EFFECT OF TEMPERATURE AND SALT CONCENTRATION ON RHEOLOGICAL BEHAVIOUR OF SURFACTIN

S. M. Salihu, A. J. Abubakar, B. Meisam, U. A. Emmanuel, and K. Y. Hassan, University of Salford, United Kingdom; and A. Y. Aminu, Ministry of Petroleum Resources Abuja, Nigeria

Abstract

Behavioural changes of surfactants due to temperature fluctuations, and its interaction with saline environment, is very common during oil and gas operations. Exhibition of transient or permanent flow behaviour is one form of these changes. Therefore, effect of temperature and ionic concentrations (salinity) on flow behaviour of sodium surfactin was experimentally investigated. ORCADA® software-controlled OFITE viscometer (Model 1100) was used to conduct steady-shear study, at 23–50 °C temperature, 0.1–1.5 molar (M) salt concentrations and 0.025–1.0 % surfactin dosages. Sodium surfactin behaves as non-Newtonian fluid, with a pseudoplastic pattern exhibited in aqueous and 0.25–1.5M saline media. Effect of changes in temperature and salinity on apparent viscosity of surfactin was surfactant-dosage dependent. Furthermore, shear-thickening effect set in at a critical shear rate of 680.9 s⁻¹, signifying flow-induced self-aggregation. Surfactant dosages 0.075 and to a lesser extent 0.1% were minimally affected by changes in temperatures, salinity and rate of shear not exceeding 680.9 s⁻¹. The findings suggest pumpability and dispersion characteristics of the biosurfactant.

Introduction

Surfactin, a biological surface-active agent (biosurfactant), produced from Bacillus subtilis is increasingly been accepted for many industrial applications including oil and gas (Al-Bahry et al., 2013; Al-Wahaibi et al., 2014; Alves et al., 2010; Bezza & Chirwa, 2015). The acceptance stem from their ease of biodegradability, less toxicity, high detergency, better foaming and wetting properties, and greater stability compared to synthetic surfactants (Bezza & Chirwa, 2015; Chen, Juang, & Wei, 2015; Inès & Dhouha, 2015). Furthermore, successful experimental and numerical study on application of surfactin in oil/gas industry for either soil bioremediation, enhanced oil recovery, and/or heavy oil transport in pipelines have been reported by many authors (Fernandes et al., 2016; Frigaard, Paso, & de Souza Mendes, 2017; Inès & Dhouha, 2015). Success of these applications centres on the ability of the surfactin to remain adhered on oil-water, gas–oil or gas–water interface, thereby hindering inter-particle cohesion hence increasing the surface area along the fluids interface. However, during industrial operations, fluids exhibits some form of transient or permanent flow behaviour due to shear, compression and/or expansion stress.
The resulting change in flow behaviour is of concern to operators. It may result to undesirable consequence such as pressure loss in pipes (Sharma, Tiwari, & Dixit, 2016) due to failure, and burn-out of equipment (such as pump) (Franck, 2004), during operations, especially at start up. This study will therefore be a tool to enhancing the performance, assessing point of surfactin failure, and investigation on relaxation of surfactin at fluids surfaces/interfaces. It also defines the extent of surfactin response to any form of shear during application, and behaviour at quiescent state. Available literature indicated that studies regarding response of surfactin to rate of shear in a solution of varying ionic strength, and at varying temperature are limited. However, many factors including temperature, hydrophobic chain length and ionic concentration have been reported to impact micellization. (Al-Bahry et al., 2013) investigated effect of incubation media and time on surfactin viscosity. Authors reported no significant changes in viscosity. (Osman, Høiland, & Holmsen, 1998) studied the effect of pH, temperature and Ca\(^{2+}\) on micropolarity and microviscosity of surfactin adopting the use of FTIR and flurometric analysis methods. Further to flow behaviour of biomolecules, (de Oliveira, Amaral, & Burkert, 2018) reported increase in apparent viscosity on addition of 1molL\(^{-1}\) NaCl salt. Range of salt concentration used does completely reflect that of produced water from oil and gas operations. Furthermore, (Zdziennicka, Krawczyk, & Jańczuk, 2018) studied the volumetric properties of Rhamnolipid and surfactin at temperatures of 293K, 303K and 313K. Additionally, (Ohadi, Dehghannoudeh, Forootanfar, Shakibaie, & Rajaee, 2018) structural and aggregation behaviour of lipopeptide biosurfactant. The authors, in all these studies, were unable to capture scenarios and conditions typical of applications in oil/gas industries. In this study, therefore, response of aqueous surfactin to rate of shear at temperature ranges of 23 to 50 °C, and at varying aqueous NaCl salt solution of 0.1–1.5 M concentration was investigated. OFI Testing Equipment (OFITE) viscometer model 1100 was used for the analysis.

**Materials and Method**

**Materials**

Sodium Surfactin (Kaneka surfactin) biosurfactant (CAS No.302933-83-1), C\(_{55-n}\)H\(_{95.5-2n}\)N\(_{7}\)O\(_{13}\)Na\(_{1.5}\), was purchased, and used as received, from Kaneka Europe Holding Company, Belgium. Aqueous solution of the surfactin was made using distilled water locally made in the Petroleum and Gas Engineering laboratory of University of Salford. Acros Organics brand (207790010/20) analytical grade univalent salt, Sodium chloride (NaCl) with 99.5% purity was purchased from Fisher Scientific, UK.

**Method**

**Sample preparation**

Aqueous solution of surfactant was prepared by measuring and directly adding 0.025, 0.05, 0.075, 0.1 0.5 and 1.0 w/v% dosages of surfactant into sample container, and with distilled water subsequently added. The mixture was vigorously agitated and stirred and allowed at least for 5 hours to completely dissolve. Surfactant dosages were adopted based on the works of (Al-Wahaibi et al., 2014; Saito, Sugai, Sasaki, Okamoto, & Ouyang, 2016; Whang, Liu, Ma, & Cheng, 2008).

Saline solutions of 0.1–1.5 M concentration were as well prepared by measuring and dissolving appropriate amount of salt into 2 litres of distilled water. The solution was well stirred using hotplate magnetic stirrer. Each concentration of the saline solution was then used to prepare surfactant solution, using the various dosages stated above.

**Measurement of rheology**

The rheological experiments were carried out using ORCADA® software–controlled OFITE viscometer (Model 1100), having a shear rate range of 0.01–1000 s\(^{-1}\) and 0.001 RPM speed accuracy. Based on its
configuration of B1, 42 ml of calibration fluid was used to first calibrate the viscometer. Input data (RPM, temperature, etc.) were then specified in the Test Builder, and RP 10B analysis model (combination of Power Law and Bingham Plastic Models) was selected. Temperature in the range of 23 °C (ambience) 30, 40 and 50 °C were inputted with an allowance of ±1 °C. 0–600 RPM were selected for the test, and units of shear stress and viscosity were then specified accordingly. Having keyed in the input data and the test analysis mode selected, 42 ml of each of dosage samples prepared was measured and poured into the sample cup and tightly screwed. “Start Test” button was entered to begin analysis, until all RPM specified were completed. The experimental set-up is shown in Figure 1.

This same procedure was repeated for all samples in saline solution, at ambient temperature of 23 °C with an allowance of ±1 °C.

**Result and discussion**

**Steady shear effect at different temperature**

Figure 2 shows plot of viscosity against rate of shear at temperatures of 23, 30, 40 and 50 °C, designated respectively by a, b, c and d. It indicates pseudoplastic behaviour (Drew, 2006; Jain, Mody, Mishra, & Jha, 2012; Mu, Li, Jia, Wang, & Zhang, 2002) of sodium surfactin across all dosages and temperature. Furthermore, three (3) plateau regions, regardless of dosage, were noticed. Low-shear region exhibiting characteristics of spherical micelles formation. The region depicts a small shear-induced decrease in viscosity below 85.1 s⁻¹ shear rate (ϒ). Moreover, within same shear rate boundary, initial viscosity (η) of 1.0% surfactin increases from 22.2-25.7 mPas (Figure 2b), when temperature was increased to 30 °C.
Conversely, viscosity of other dosages decreases within same range of temperature and \( \gamma \). The trend became highly dosage dependent at 40 and 50 °C. Beyond \( 85.1 \text{ s}^{-1} \), reorientation of surfactin molecules became strongly shear-dependent. \( \gamma \) was sufficiently high to prevent surfactin chains from undergoing any form of self-aggregation.

\[ \text{Figure 2 Viscosity vs shear rate of variable surfactin dosages at (a) 23 °C (b) 30 °C (c) 40 °C, and (d) 50 °C} \]

Consequently, viscosity (\( \eta \)) decreases continuously with increasing \( \gamma \), depicting a continuous irreversible shear-thinning behaviour (Lutz-Bueno, 2016; Rivero, Gouveia, Müller, & Sáez, 2012) across all dosages. This form of behaviour is a very useful property for adsorptivity (Schroyen, Gunes, & Vermant, 2017), drilling fluid additives, and dispersant for flow assurance (Frigaard et al., 2017).

Pseudoplastic behaviour reached a minimum at critical \( \gamma \) of 680.9 s\(^{-1}\), and shear-thickening behaviour set in beyond this value. The shear-thickening increase as the temperature increase which is visibly evident in Figure 2c and d. Increasing temperature perhaps led to increased micelles concentration and consequently formation of larger aggregates (rod-like micelles). It is worthy to note that dosages 0.075 and 0.1% are least affected by changes in temperature and shear rate.

**Dosage effect at zero-shear**

To clearly understand effect of dosage on viscosity at different temperatures, plots of surfactin dosages used in the study were made against apparent viscosity at zero shear (\( \eta_0 \)). Figure 3 generally depicts a monotonic response of viscosity to change in surfactin dosage. At ambient and 50 °C, the \( \eta_0 \) increases with increasing dosages up to critical dosages of 0.075 and 0.1%. Conversely, temperatures 30 and 40 °C decreases the \( \eta_0 \) as the dosage increase. However, irrespective of the temperature change, there seems a
convergence at 0.075 and 0.1% dosage. This indicates that, changes in temperature is unable to induce any form of molecular chain mobility of structures (Alves et al., 2010) at critical dosages. It could as well be an indication of range of the surfactant’s critical micelle concentration (CMC).

Temperature effect on apparent viscosity

Temperature fluctuations is a common occurrence associated with oil and gas operations. It therefore become critical to study response of surfactin to these fluctuations at different shear rate. Consequently, effect of temperature on viscosity for different dosages of surfactin at different rate of shear was evaluated. It is obvious in Figure 4 (a and b) that temperature increase resulted in simultaneous breakage and realignment of the surfactin network at zero-shear. Additionally, each dosage exhibited peculiar specific apparent viscosity response to changes in temperature.

Surfactin dosage 0.025% depicted significant monotonic decrease while 0.05% depicted a monotonic increase behaviour. Additionally, 30 °C caused viscosity decrease effect in both a and b. Of interest (in figure3b) is the sharp decrease in apparent viscosity ($\eta_{\text{app}}$) from 14.9 to 7.6 mPas when temperature increased from 23 to 30 °C. The increase induced a breakage and realignment of the surfactin network. Though it reduced viscosity across the dosage, it could not sustain the network deformation (Kamal, 2016). At higher rate of shear, however, temperature effect became less significantly visible indicating that the molecular rearrangement was shear-controlled.
Conversely, temperature increase at zero-shear resulted in molecular aggregation on surfactant dosages 0.075 and 1.0% (Figure 5a and b). The effect, unlike at zero-shear, was less significant at higher rate of shear.

Figure 6a indicates that increasing temperature results in continuous formation of large aggregates at zero-shear. This is evident by the continuous increase in $\eta_{\text{app}}$. Furthermore, $\eta_{\text{app}}$ of 1.0% dosage increased to a value of 25.7 mPas at 30°C (Figure 6b). But with shear rate increase, $\eta_{\text{app}}$ became less sensitive to temperature. At 680 s$^{-1}$, dosage 1.0% became highly shear rate induced that the apparent viscosity value was close to unity.

These affirm that apparent viscosity of surfactin is more dosage and shear rate dependent than it is on temperature, particularly at high shear rate. Thus, surfactin like other biosurfactants, such as extracellular polysaccharides produced from glycerol (Alves et al., 2010), thermo-rheologically stable.

Steady shear effect at different salt concentration

Performance of biosurfactant for oil/gas application is dependent on their behaviour in solutions like that of formation water. Of particular significance is the microviscosity, and how it is affected by the micellar phase, in terms of the solubilizing properties of the micellar core (Li, Zou, Ye, & Mu, 2009). The morphology and molecular architecture of the surfactant may be responsible for this microviscosity effect. Organic or inorganic salts, cosurfactants and/or strongly binding counter ions were reported to have induced sphere-to-wormlike transition in nanostructure of ionic surfactants. This may suggest that exposing
sodium surfactin to saline environment will impact on micellization hence its interfacial property during adsorption (Schroyen et al., 2017) and rheology. Change in ionic concentration of dispersion medium may increase or decrease the size and shape of a micelle. Li (Li et al., 2009), hypothesized that there exist two opposing tendencies in the formation of micelles of ionic surfactants: (1) removal of hydrocarbon chains from water favours aggregation; and (2) electrostatic repulsions between the ionic head groups opposes aggregation (Shrestha & Aramaki, 2008). Knoblich (Knoblich et al., 1995), reported surfactin micelle to be spherical, ellipsoidal and/or cylindrical with a non-homogeneous size distribution at pH 7, 9.5, and 12. Additionally, Liu (Liu, Mbadinga, Yang, Gu, & Mu, 2015) also reported that cylindrical micelles do transformed into spherical and/or ellipsoidal micelles of smaller sizes when exposed to saline solution environment of 100mM NaCl and 20mM CaCl$_2$. These are in line with the findings in this study shown in Figure 7.

**Figure 7 Viscosity vs shear rate as a function of surfactin dosage at 0.1M salt concentrations**

0.1M NaCl salt concentration had a lytic effect on $\eta_{app}$ of surfactin molecule. At this concentration, there was increased electrostatic repulsion between surfactant head group which limit micellar growth to small finite particle sizes (Li et al., 2009; Lutz-Bueno, 2016). It consequently led to zero viscosity at shear rate of up to 510 s$^{-1}$ across most dosages. Nevertheless, dosage 0.075% maintained relatively constant but higher $\eta_{app}$. Beyond 510 s$^{-1}$ $\gamma$, attractive Van der Waals force between the tails in the micellar became shear induced. Accordingly, that resulted to molecular self-aggregation that caused to shear-thickening behaviour.

Flow behaviour of surfactin at increased salt concentration is like those reported in figure 1. However, increased ionic concentration resulted in increased $\eta_{app}$ at zero-shear and constant temperature. For example, $\eta_o$ of 1.0% surfactin dosage increased from 22.2 to 25.8 mPas at 0.25 M salt concentration (Figure 8a). It further increased to 36.9 mPas at 0.5 M in Figure 8b. Increasing salt concentration could have favoured removal of hydrocarbon chains from water. Consequently, it increased electrostatic coalescence between the hydrophilic group, which results in molecular self-aggregation. This effect however became dosage-dependant as the salt concentration increased to 1.0 and 1.5 M (Figure 8c and d).
Flow behaviour became strongly shear-induced above 850.1 s⁻¹, with surfactin exhibiting continuous shear-thinning characteristics. Increase in salinity consequently led to increased electric charge density of the polar shell formed at surface of the micelle (Lutz-Bueno, 2016). This results to upsurge of electrostatic repulsions between head groups, which consequentially increased pseudoplastic behaviour of the surfactin. Unlike at zero salt concentration, 680.9 s⁻¹ critical shear was strongly dosage dependent. Figure 8a shows that η_{app} of 0.075% dosage continue to decrease with increasing rate of shear to a near zero value. To stabilize surfactant in ionizing solutions, counter ions bind to the micelles and thereby screening the electrostatic repulsion, a process that influence micellization. This phenomenon has been occurring with the surfactant with change in salinity and dosage. It signifies that the ionic concentration increase influenced the molecular mobility of the surfactant. Though the behaviour was generally pseudoplastic, it was shear-induced, especially at high shear rate.

**Conclusion**

Response of sodium surfactin to different rate of shear was evaluated, taking into consideration surfactin dosage, salt concentration and temperature. Based on the findings in this study, sodium surfactin behaves as non-Newtonian fluid, with pseudoplastic flow pattern. Effect of changes in temperature on apparent viscosity of surfactin was largely shear rate dependent. Conversely, change in salt concentration was both dosage and shear rate dependent. Furthermore, shear-thickening effect set in at a critical shear rate of 680.9s⁻¹, signifying flow-induced self-aggregation. Surfactant dosages 0.075 and to a lesser extent 0.1% were minimally affected by changes in temperatures, salinity and rate of shear not exceeding 680.9s⁻¹. The results suggest pumpability and dispersion characteristics of sodium surfactin, hence its suitability in oil and gas applications.
Acknowledgement

The sponsorship of Nigeria’s Petroleum Technology development Fund (PTDF) is duly acknowledged and appreciated by the authors.

References


