CHEMICAL ENGINEERING TRANSACTIONS

VOL. 56, 2017

A publication of
AIDIC
The Italian Association
of Chemical Engineering
Online at www.aidic.it/cet

Guest Editors: Jiří Jaromír Klemeš, Peng Yen Liew, Wai Shin Ho, Jeng Shiun Lim
Copyright © 2017, AIDIC Servizi S.r.l.,
ISBN 978-88-95608-47-1; **ISSN** 2283-9216

DOI: 10.3303/CET1756208

Influence of Silicon Oxide and Aluminum Oxide Nanoparticles on Air and CO_2 Foams Stability in Presence and Absence of Oil

Nurudeen Yekeen*, Muhammad A. Manan, Ahmad Kamal Idris, Ali Mohamed Samin, Abdul Rahim Risal

Department of Petroleum Engineering, Faculty of Chemical and Energy Engineering,Universiti Teknologi Malaysia, 81310 Johor Bahru, Malaysia
peteryekeen@yahoo.com

One of the major issues in foam application for enhanced oil recovery (EOR) is the foam stability in presence and absence of oil. In this study, a systematic experimental study of the bulk and bubble scale stability of air and CO_2 foams stabilised by sodium dodecyl sulphate (SDS) and nanoparticles were conducted. Foam-oil interactions were further study in etched glass micromodel in order to investigate and compare the foam performance at static and dynamic conditions. Influence of nanoparticles hydrophobicity and oil types on foam behaviors were assessed. Static bulk and bubble-scale experiments were conducted with KRÜSS dynamic foam analyser while the flow characteristics experiments were conducted in etched glass porous medium. Results show that the foam half-life increased while the size of generated bubbles decreased with the presence of nanoparticles in the surfactant solution. Successful propagation of nanoparticles-SDS foam through capillary snap-off and lamellae division was observed in presence of oil in the porous medium. Foam stability decreases with decreasing oil viscosity and density. Except for hydrophobic aluminum oxide nanoparticles with contact angle of 118.19°, the static and dynamic stability of the air and CO_2 foams increased with increasing nanoparticles hydrophobicity. The addition of nanoparticles into the surfactant solution considerably improved foam stability due to the adsorption and aggregation of the nanoparticles at the thin lamellae and plateau border. This prevents liquid drainage and film thinning by increasing film elasticity and film strength from 23.2 µm to 136 µm. It can be concluded from this study, that stable air and CO_2 foams can be generated with nanoparticles-surfactant mixed systems in absence and presence of oil with favourable nanoparticles hydrophobicity.

1. Introduction

Gas injection enhanced oil recovery (EOR) process usually results in gravity override, gas segregation, viscous fingering and channelling through the high permeability streaks (Farajzadeh et al., 2012). This is due to the low viscosity and density of gas compared to oil and water. Foam, a colloidal dispersion of gas in liquid helps to control gas mobility by increasing the apparent viscosity of the displacing fluid and reduced the relative permeability of the gas phase. Foams are thermodynamically unstable and require the use of surface active agents such as surfactants for their continuous generation, stability and propagation in porous media. Surfactants has been employed as the conventional method of foam stabilisation for several decades (Rossen, 1996). Surfactant stabilised foams are unable to maintain their stability for a long time at high salinity, temperature and in presence of resident reservoir brines and oil (Adkins et al., 2007). The rate of surfactant adsorption on rock surfaces can be very high.

Foams stabilised by nanoparticles-surfactant mixtures recently attracted an attention for potential applications in EOR. Results of previous studies show that these foams demonstrated high initial foamability and long-time stability (Sun et al., 2014). This can be attributed to the irreversible adsorption of nanoparticles on surface of their bubbles (Singh and Mohanty, 2015). Surfactants as the foaming agents also help to improved oil recovery through interfacial tension and capillary forces reduction (Osei-Bonsu et al., 2015). The foams are expected to

Please cite this article as: Yekeen N., Manan M.A., Idris A.K., Samin A.M., Risal A.R., 2017, Influence of silicon oxide and aluminum oxide nanoparticles on air and co2 foams stability in presence and absence of oil, Chemical Engineering Transactions, 56, 1243-1248
DOI:10.3303/CET1756208

be stable in porous formation at high salinity, temperatures and presence of oil since nanoparticles as the stabilising components of the foams are solids.

Silicon oxide (SiO_2) nanoparticles are normally used for improving foam stability due to their little retention in porous media. There is an emerging interest in application of aluminium oxide as foam-stabilising agents for EOR purpose. Two major factors influencing the performance of SiO_2-SDS and Al_2O_3-SDS foams in EOR are the presence of oil and the nanoparticles hydrophobicity. Results of previous studies show that oil has an adverse effect on the static and dynamic stability of foams (Osei-Bonsu et al., 2015). Unstable foams can also be formed at very low (too hydrophilic) and very high (too hydrophobic) contact angles (AttarHamed et al., 2014). Despite these results, the influence of nanoparticles hydrophobicity and oil presence on the performance of SiO_2-SDS and Al_2O_3-SDS foams is not yet explicit. In several previous studies, nanoparticles-surfactant foam stability was only examined by monitoring the changes in height of generated foam in vertical columns over time. The stability of the foam at the bubble scale, and the translation of the foam bulk and bubble level properties into in-situ behaviour in porous media have not been investigated and compared. In this study, the influence of SiO_2 and Al_2O_3 nanoparticles on the static and dynamic stability of SiO_2-SDS and Al_2O_3-SDS foams in absence and presence of oils will be investigated. The foam flow properties and foam-oil interaction at the pore scale will be investigated in the etched glass micromodels. The mechanisms of foam stabilisation by nanoparticles will be investigated and discussed.

2. Materials and methods

2.1 Materials

Sodium dodecyl sulphate (0.3 wt%), two kinds each of SiO_2 and Al_2O_3 nanoparticles (1.0 wt%) were used as the foaming and stabilising agents in this study. The two kinds of silica nanoparticles were; hydrophilic SiO_2 nanopowder from U.S research nanomaterials inc. USA and a modified SiO_2 nanopowder (50 % methyl capped, 50 % SiOH) from walker chemicals Co., Ltd. Germany. The Al_2O_3 nanopowders (hydrophilic and hydrophobic) were obtained from Skyspring nanomaterials Inc. USA. The nanoparticles hydrophobicity was determined by contact angles measurement. The basic properties of the nanoparticles in terms of type, size, specific surface area (SSA) and the contact angles are listed in Table 1

Four model oils were used to investigate foam stability in presence of oils. These include; normal decane ($C_{10}H_{22}$) and normal hexadecane ($C_{10}H_{16}$) (from Sigma-Aldrich), paraffin liquid (from Labchem) and West Lutong crude oil (From Sarawak oil field in Malaysia). The viscosities of the oils were measured with RST rheometer (Brookfield Engineering, USA) and the density was measured with pycnometer. Surface and interfacial tensions were measured with Kruss tensiometer (Kruss GmbH, Hamburg) using a Du Nuoy ring method. All measured properties were carried out at 25 °C. The properties of model oil in terms of surface viscosity, density and surface tension are listed in Table 2.

Table 1: Properties of the SiO_2 and Al_2O_3 nanoparticles used for the experiment

Types	Size (nm)	Contact angles	SSA (m^2/g)
SiO_2 (hydrophilic)	15 - 20	52.17°	170 - 200
SiO_2 (modified)	12	88.48°	130 - 170
Al_2O_3 (hydrophilic)	20	30.94°	230 - 400
Al_2O_3 (hydrophobic)	80	118.19°	-

Table 2: Properties of oils used for the experiment

Oil	Viscosity (cp)	Density (g/cm^3)	Surface tension (mN/m)
Hexadecane	3.334	0.7671	25.30
Decane	0.936	0.7253	21.08
Paraffin	20.899	0.8295	28.02
Crude	10.016	0.8283	27.04

2.2 Bulk and bubble scale stability experiments

The bulk and bubble scale foam stability experiments were performed using KRÜSS dynamic foam analyser DFA100 (KRÜSS GmbH – Germany). The foam was generated in a tempered glass column of height 250 mm and diameter 40 mm by gas sparging (from electronic gas flow control) through porous filter plate (40 - 100µm in a fixed amount of surfactant or nanoparticles-surfactant solution (50 cm^3) at a fixed gas flow rate of 0.3 L/min. For foam stability in presence of oil, 5.0 vol% of oil was used. The oil was added to the foaming agent before gas sparging. The amount of oil was calculated as a volume fraction of the foaming agent solution. The pump time was set for 12 s and the gas flow stopped automatically after 12 s. The foam generation set up was connected to a computer which serves as the data acquisition and monitoring units. Foam structure with regards to the bubble size and its distribution were measured with foam structure modules. The foam stability was evaluated from the half-life, normalised foam height and the bubble size distribution.

2.3 Foam flow characteristics experiments in presence of oil in etched glass micromodel

The micromodel for the foam flow process consists of micro-channels and a pore network of circular posts with sizes (200 µm, 600 µm and 800 µm) representative of reservoir grains. The grains were arranged to create pores of (~ 200 − 800 µm) in diameter and pore throats of sizes (~ 100 - 400 µm) with depth of 100 µm. The micromodel was designed this way in order to be able to observe how the generated foam was able to migrate through pores of varying sizes and pore throats. The total chip dimension is 60 × 160 mm, with a micro etched network region of 45 × 140 mm. The etched glass substrate was bonded to a blank cover glass plate by bringing them into contact and heating to 700 °C. The temperature was allowed to drop to the atmospheric temperature. A Leica EZ4 HD stereo microscope (Leica Microsystems Switzerland Limited) was used to capture the changes in foam structure over time. The oil was injected into the micromodel at a flowrate of 0.5 mL/h (0.0083 mL/min) with syringe pump followed by the pre-generated CO_2 foam injection.

3. Experimental results

3.1 Bulk and bubble scale experimental results

Table 3 shows the half-life of the air-foams and CO_2-foams generated in absence and presence of nanoparticles as determined from the bulk foam experiments. The higher the foam half-life, the more stable the foam and vice versa. The half-life of the air-foams increased from 63 min in the absence of nanoparticles to 140 min (122.22 %), 154 min (144.44 %) and 165 min (161.91 %) in presence of 1 wt% hydrophilic Al_2O_3, hydrophilic SiO_2 and modified SiO_2 nanoparticles. For CO_2 foam, the half-life of CO_2 foam increased from 36 min in the absence of nanoparticles, to 99 min (175 %), 110 min (205.56 %) and 123 min (241.67 %) in presence of hydrophilic Al_2O_3, hydrophilic SiO_2 and modified SiO_2 nanoparticles.

Figure 1 shows the influence of oil on air-foam and CO_2-foam bulk-scale stability (half-life). The results show that the presence of oil has a destabilising effect on the stability of SDS and nanoparticles-SDS foams.

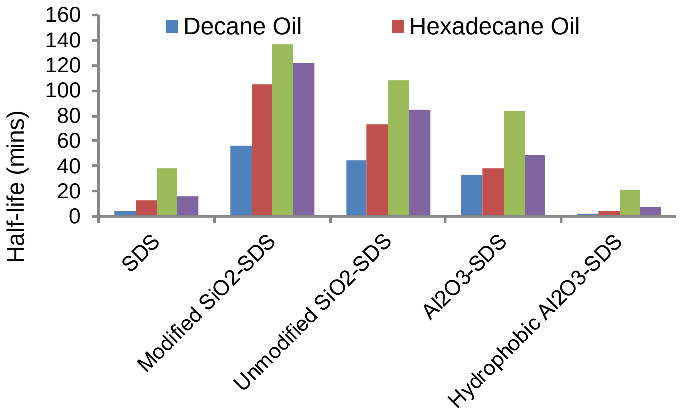


Figure 1: Improvement in foam stability (half-life) by nanoparticles in presence of oil

Table 3: Half-life in absence of oil.

Foaming agents	Half-life CO_2-foam	Half-life Air-foam
SDS only	36	63
SiO_2-SDS	110	154
Al_2O_3-SDS	99	140
Modified SiO_2-SDS	123	165
Hydrophobic Al_2O_3-SDS	45	80

The foam stability decreased with decreasing oil viscosity and density. Normal decane ($C_{10}H_{22}$) with the lowest viscosity and density produced the highest destabilising effect on the foams. Paraffin oil with the highest viscosity and density produced the least destabilising effect. The order of destructive effects of oil on the foam stability is Decane > Hexadecane > Crude oil > Paraffin. The foam stability increased with nanoparticles addition in presence of oil. In presence of paraffin oil, the half-life of air-foam increased from 38 to 84 (121.05 %), 108 (184.21 %) and 137 (260.53 %) with the addition of hydrophilic Al_2O_3, hydrophilic SiO_2 and modified SiO_2 nanoparticles. For the hydrophobic Al_2O_3 nanoparticles, the change in foam stability (half-life) was not significant due to the nanoparticles hydrophobicity.

This result is further supported by plots of normalised height and foam volume versus time in Figure 2. The plotted graphs shows that the foam volume and normalised height for SiO_2-SDS and Al_2O_3-SDS foam was higher than that of SDS foam in presence of decane. The bubble size distribution of air-foams after 60 min in Figure 3(a) and (b) further confirms the high stability of nanoparticles-SDS foam compared to SDS foam. In the absence of nanoparticles (Figure 3(a)), the bubbles were bigger and collapses faster due to high rate of film thinning and foam drainage. In presence of SiO_2 nanoparticles (Figure 3(b)), the bubbles were many and smaller in size, signifying slower rate of bubbles coalescence and high foam stability.

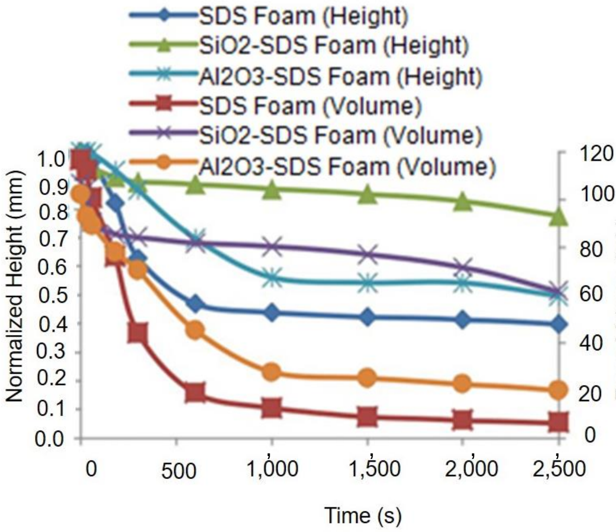


Figure 2: Normalised foam height and foam volume of SDS and nanoparticles-SDS foams with respect to time

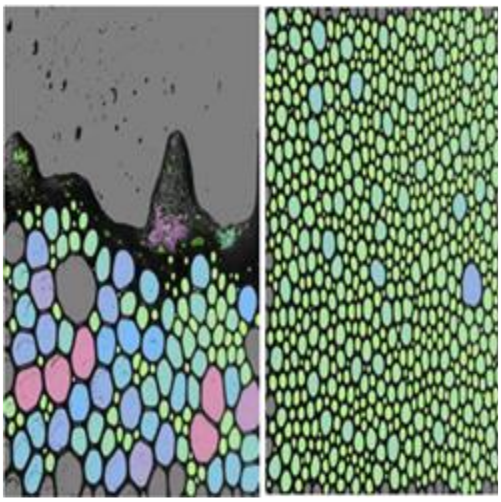

(a) (b)

Figure 3: Bubble size distribution of (a) SDS-stabilised foam and (b) SiO_2-SDS stabilised foam after 60 min

The result is in conformity with the results of previous studies that oils with low viscosity and densities are more detrimental to foam stability (Vikingstad et al., 2005). The low stability of foam in presence of oil with low viscosity and density can be attributed to the increasing entering and spreading of oil at the foam lamellae (Yekeen et al., 2016). The increasing entering and spreading of oil on the film interface forces liquid out of the films into the plateau borders. The intensity of oil droplets dispersion in the bulk foam also increases with the reducing oil viscosity and density (Osei-Bonsu et al., 2015). Foam stability reduces as a result of the increasing interaction between the oil and the foam at the gas-liquid interface. In terms of the molecular weight, decane and shorter alkanes will solubilise in the micelles aggregates due to their smaller molecular elements. Hexadecane are too large to be solubilised in the micelles and thereby have less ability to be transported out of the foam (Vikingstad et al., 2005). The high stability of hexadecane compared to decane can be ascribed to a reduction in the film thinning rate due to the presence of long chain alkanes and the accumulation of oil droplets in the plateau borders.

3.2 Foam flow characteristics in etched glass micromodel

The etched glass micromodel described in Section 2.3 was used to investigate foam flow characteristics in presence of oil in porous medium. Figure 4 shows the condition of the SDS-foam and the hydrophilic SiO_2- SDS foam in presence of paraffin oil. There was emulsification of oil into smaller drops as the foam contacts the resident oil. This allows ready access of oil into the foam structure. In the absence of nanoparticles (Figure 4(a)), there was an extensive imbibition of the emulsified oil into the foam lamellae which resulted in rapid film thinning. The emulsified oil droplets continue to move along further lamellae into the plateau borders resulting in faster rate of bubble coalescence and coarsening. In the presence of nanoparticles (Figure 4(b)), finer oil emulsions were formed. Finer oil emulsions were reported from previous studies to results in stable foams (Wasan et al., 1994). The extent of entry and imbibition of the emulsified oil into the foam structure was very low, due to the adsorption and aggregation of SiO_2 nanoparticles into the foam lamellae and plateau borders. The inability of the oil to penetrate into the foam lamellae and plateau borders enables the oil to be dragged along and sweep-off the pore walls by the foam. There is lower residual oil in presence of SiO_2-SDS foams compared to the SDS foams. The SiO_2-SDS foams also propagate successfully in the pore through continuous foam generation mainly in form of snap-off and lamellae division mechanisms as observed in Figure 4(b).

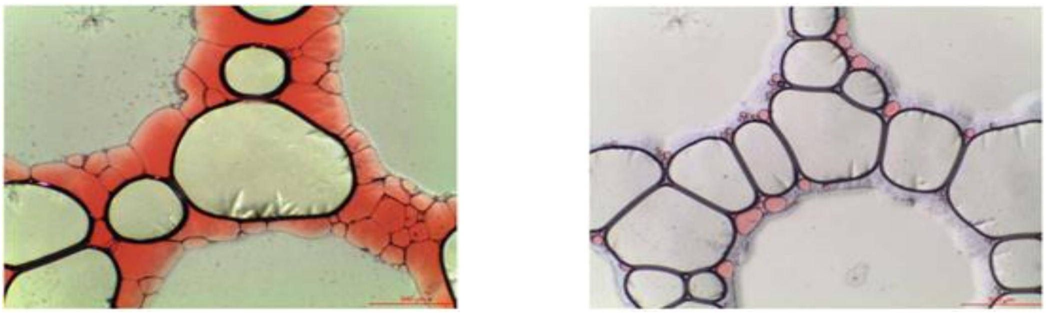

(a) (b)

Figure 4: Foam flow process in presence of paraffin oil in etched glass micromodel for (a) SDS-stabilised foam and (b) SiO_2-SDS stabilised foam

3. Mechanisms of foam stabilisation by nanoparticles

3.1 The adsorption and aggregation of nanoparticles at the gas-liquid interface of foams

Figure 5 shows that there is an adsorption and accumulation of the nanoparticles at the thin lamellae of Al_2O_3-SDS foam. The considerable resistance of nanoparticles-SDS stabilised air-foam and CO_2-foam to coalescence observed in presence and absence of oil in this study is due to the irreversible adsorption of the nanoparticles at the gas-liquid interface of the generated foam. The adsorbed nanoparticles aggregated at the foam lamellas and plateau borders to promote foam stability by delaying the rate of film thinning, liquid drainage, bubble coalescence and coarsening. For the hydrophobic Al_2O_3 nanoparticles with no significant improvement in stability of SDS foam. It is likely that the nanoparticles contact angle (118.19) was too high to generate stable foams. At very high contact angle, instead of promoting foam stability by their adsorption and accumulation at foam lamellae and foam network, the nanoparticles remain dispersed in either the aqueous phase or the air and CO_2 phase (Attarhamed et al., 2014). The dispersed nanoparticles increased the influence of surface forces like Vander Waals and gravity forces on the interfacial films to produce unstable foams.

3.2 Increase in film thickness and strength

Figure 6 shows the images of SDS bubbles and that of hydrophilic SiO_2/SDS air-foam (with 1 wt% SiO_2 concentration) after 60 min as observed under the Leica EZ4 Microscope. The biggest film thickness for the SDS foam is 23.2 µm in absence of nanoparticles (Figure 6(a)). In presence of 1 wt% SiO_2 nanoparticles (Figure 6(b)), the film thickness is 136 µm (486.21 % more than that of SDS). The SDS bubbles also collapses faster with time. After 60 min, the SDS bubbles sizes became bigger with an irregular shape. For SiO_2-SDS foam, the bubbles shape remains either spherical or ellipsoidal and the film thickness remains the same. The increase in film thickness of SiO_2/SDS foam is due to the formation of an interfacial shield around the bubble surface by the aggregated nanoparticles at the bubble interface, plateau borders and foam network. This action, besides prevention of film thinning and bubble coalescence improved surface dilatational viscoelasticity of the nanoparticles/SDS foam. It further enables the foam lamellae to withstand the pressures caused by gas diffusion out of small bubbles during Ostwald ripening and film stretching.

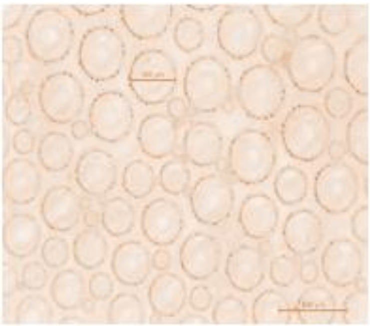
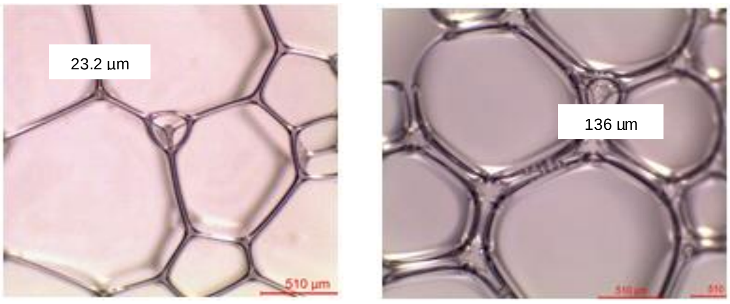


Figure 5: Foam image of Al_2O_3-SDS foam showing aggregation



(a) (b)

Figure 6: Foam image showing film thickness for (a) SDS-stabilised foam and (b) SiO_2-SDS stabilised foam

4. Conclusions

This paper studies the influence of Al_2O_3 and SiO_2 nanoparticles on the static and dynamic stability of air and CO_2 foams in absence and presence of normal decane, normal hexadecane, paraffin and crude oil with differing viscosity and density. The following conclusions can be drawn from this study.

1. The presence of nanoparticles in the surfactant solution increased the foam half-life, film thickness and decreases the bubble sizes and prevents spreading of oil at the foam lamellae.
2. The foam stability decreases while the size of generated bubbles increases with decreasing oil viscosity and density. However there was an improvement in stability of SDS foam in presence of oil with the addition of nanoparticles.
3. Excluding the hydrophobic Al_2O_3-SDS foam with unfavourable contact angle (118.19^o) for foam generation, foam stability generally increased with increasing nanoparticles hydrophobicity due to high particle detachment energy at favourable contact angle.
4. The nanoparticles-SDS foams can propagate successfully in the presence of oil in porous media by snap-off and lamella division mechanisms.
5. Adsorption and aggregation of nanoparticles at the foam lamellae and increase in film thickness are the major mechanisms of foam stability improvement by nanoparticles in absence and presence of oil.

References

Adkins S.S., Gohil D., Dickson J.L., Webber S.E., Johnston K.P., 2007, Water-in-carbondioxide emulsion stabilized with hydrophobic silica particles, Physical Chemistry Chemical Physics 9, 6333-6343.

Attarhamed F., Zoveidavianpoor M., Jalilavi M., 2014, The Incorporation of Silica Nanoparticle and Alpha Olefin Sulphonate in Aqueous CO2 Foam: Investigation of Foaming Behavior and Synergistic Effect, Petroleum Science and Technology 32, 2549-2558.

Farajzadeh R., Andrianov A., Krastev R., Hirasaki G.J., Rossen W.R., 2012, Foam–oil interaction in porous media: Implications for foam assisted enhanced oil recovery, Advances in Colloid and Interface Science 183–184, 1-13.

Osei-Bonsu K., Shokri N., Grassia P., 2015, Foam stability in the presence and absence of hydrocarbons: From bubble-to bulk-scale, Colloids and Surfaces A: Physicochemical and Engineering Aspects 481, 514-526.

Rossen W.R., 1996, Foams in enhanced oil recovery, Surfactant Science Series, Marcel Dekker, New York, United States, 413-464.

Singh R., Mohanty K.K., 2015, Synergy between Nanoparticles and Surfactants in Stabilizing Foams for Oil Recovery, Energy and Fuels 29, 467-479.

Sun Q., Li Z., Li S., Jiang L., Wang J., Wang P., 2014, Utilization of Surfactant-Stabilized Foam for Enhanced Oil Recovery by Adding Nanoparticles, Energy & Fuels 28, 2384-2394.

Vikingstad A.K., Skauge A., Høiland H., Aarra M., 2005, Foam–oil interactions analyzed by static foam tests, Colloids and Surfaces A: Physicochemical and Engineering Aspects 260, 189-198.

Wasan D., Koczo K., Nikolov A., 1994, Mechanisms of aqueous foam stability and antifoaming action with and without oil: a thin-film approach, Advances in Chemistry Series 242, 47-47.

Yekeen N., Idris A.K., Manan M.A., Samin A.M., 2016, Experimental Study of Influence of Silica Nanoparticles on the Bulk Stability of SDS-Foam in Presence of Oil, Journal of Dispersion Science and Technology, 416-424.