

Edith Cowan University
Research Online

ECU Publications Post 2013

2020

Synergistic effect of hydrophilic nanoparticles and anionic surfactant on the stability and viscoelastic properties of oil in water (o/w) emulsions; Application for enhanced oil recovery (EOR)

Sarmad Al-Anssari
Edith Cowan University

Zain-UL-Abedin Arain

Haider A. Shanshool

Alireza Keshavarz
Edith Cowan University

Mohammad Sarmadivaleh

Follow this and additional works at: <https://ro.ecu.edu.au/ecuworkspost2013>

 Part of the [Chemical Engineering Commons](#)

Al-Anssari, S., Arain, Z. U. A., Shanshool, H. A., Keshavarz, A., & Sarmadivaleh, M. (2020). Synergistic effect of hydrophilic nanoparticles and anionic surfactant on the stability and viscoelastic properties of oil in water (o/w) emulsions; application for enhanced oil recovery (EOR). *Journal of Petroleum Research and Studies*, 10(4), 33-53.
<https://jprs.gov.iq/index.php/jprs/article/view/366>

This Journal Article is posted at Research Online.
<https://ro.ecu.edu.au/ecuworkspost2013/9873>



Synergistic effect of hydrophilic nanoparticles and anionic surfactant on the stability and viscoelastic properties of oil in water (o/w) emulsions; application for enhanced oil recovery (EOR)

Sarmad Al-Anssari^{1,2,3*}, Zain-UL-Abedin Arain¹, Haider Abbas Shanshool², Alireza Keshavarz³ Mohammad Sarmadivaleh¹

¹WA School of Mines: Minerals, Energy and Chemical Engineering, Curtin University, Perth, Australia

²Department of Chemical Engineering, College of Engineering, University of Baghdad, Iraq

³School of Engineering, Edith Cowan University, Joondalup, Australia

*Corresponding Author E-mail: sarmadfoad@yahoo.com;
sarmad.al-anssari@postgrad.curtin.edu.au

Abstract:

With the rapidly increased global energy demand, great attention has been focused on utilizing nanotechnology and particularly nanofluids in enhanced oil recovery (EOR) to produce more oil from low-productivity oil reservoirs. Nanofluid flooding has introduced as one of the promising methods for enhanced oil recovery using environment-friendly nanoparticles (NPs) to be as an innovative-alternative for chemical methods of EOR. This work investigates the synergistic effects of anionic surfactant and hydrophilic silica nanoparticles on the stability and the mechanical behavior of oil in water (O/W) emulsions for their application in EOR.

To achieve this, an extensive series of experiments were conducted at a wide range of temperatures (23 – 70 °C) and ambient pressure to systematically evaluate the stability and the viscoelastic properties of the oil in water (O/W) emulsion with the presence of hydrophilic silica nanoparticles and an anionic surfactant. In this context, the initial oil to water volume ratio was 25:75. Sodium dodecylsulfate (SDS) was used as the anionic

surfactant and n-decane was used as model oil. A wide concentration ranges of NPs (0.01 – 0.2 wt%) and surfactant (0.1 – 0.3 wt%) were used to formulate different emulsions. For stability measurements, a dynamic light scattering and zetasizer were used to measure the particle size distribution and zeta potential respectively. Creaming and phase behaviors were also investigated. The viscoelastic measurements were conducted using Discovery Hybrid Rheometer.

Results show that in the presence of surfactant, and NPs mitigates the coalescence of dispersed oil droplets giving high promises in EOR applications. Further, over the tested range of temperatures, the viscosity of O/W emulsion remains stable which indicates thermal stability.

Despite studies examining the use of nanoparticle-surfactant combination in sub-surface applications, no reported data is currently available, to the best of our knowledge, about the potential synergistic effect of this combination on the stability and viscoelastic properties of O/W emulsion. This study gives the first insight on nanoparticle-surfactant synergistic effect on oil in water (O/W) emulsion for EOR applications.

التأثير المشترك للجسيمات النانوية ومثبطات الشد السطحي الايونية على حالة الاستقرار وخواص اللزوجة لمستحلبات الزيت في الماء: تطبيق لعمليات تحسين انتاج النفط الخام

الخلاصة:

مع تزايد الطلب العالمي للطاقة، برزت الحاجة وبقوة لاستخدام تقانة النانو وخصوصا المحاليل النانوية في تطبيقات تحسين انتاج النفط الخام لأننتاج المزيد من الخام من الحقول النفطية قليلة الإنتاجية. عملية حقن المحاليل النانوية في الابار النفطية سبق ان قدمت على انها واحدة من الطرق الواعدة لتحسين انتاج النفط الخام باستخدام مواد بحجم النانو صديقة للبيئة ولتكون بديل مبتكر للعمليات الكيماوية في تحسين انتاج النفط الخام. هذه الدراسة تبحث التأثير المتأزر (المتداخل والمشارك) لمواد كسر الشد السطحي الايونية مع جسيمات النانوسيليكيا المبتلة بالماء على حالة الاستقرار وخواص اللزوجة لمستحلب النفط في الماء وتأثير ذلك على تطبيقات تحسين انتاج النفط الخام.

لتحقيق هذا الغرض، تم اجراء سلسلة من التجارب المختبرية في مدى واسع من درجات الحرارة (23 – 70) درجة مئوية وفي الضغط الجوي لتقييم حالة الاستقرار وخواص اللزوجة لمستحلب النفط في الماء بوجود الجسيمات النانوية ومواد كسر الشد السطحي الايونية. في هذه الدراسة، نسبة المستحلب المحضر كانت ربع زيت الى ثلاث ارباع ماء. صوديوم دوديكايل سلفيت استخدم بصفة كاسر شد سطحي ايوني والنورمل ديكان استخدم بصفة زيت نموذجي. مدى واسع من تراكيز النسب الوزنية للكاسر الايوني (0.1 – 0.3) والنانو سيليكيا (0.01 – 0.2) استخدمت لتحضير مستحلبات مختلفة.

في قياسات الاستقرار، مقياس تفكك الضوء الديناميكي ومقياس جهد زيتا استخدمنا في حساب توزيع حجم الجسيمات وجهد زيتا (شحنة السطح) على التوالي كذلك تم دراسة عملية التلبد والالتحام والتفشد في المستحلب وتصرف الطور في مختلف التراكيز ودرجات الحرارة. قياسات اللزوجة أجريت باستخدام مقياس اللزوجة نوع ديسكفري المطور.

أظهرت النتائج المتحصلة انه وبوجود كواسر الشد السطحي الايونية تقوم جسيمات السليكا النانوية بخفض الشد السطحي بشكل أعمق بالتأثير مما تقوم به الكواسر منفردة كما يخفف إمكانية التهام قطرات الزيت المنتشرة في المستحلب مما يعطيه إمكانية تطبيق كفو في عمليات تحسين انتاج النفط الخام. بالإضافة الى ذلك فانه وضمن حدود درجات الحرارة المستخدمة في الدراسة، فان لزوجة المستحلب تبقى ثابتة مع تغيير درجات الحرارة بوجود مزيج النانو سيليكيا والكاسر الايوني مما يعطيه صفة الاستقرار الحراري. على الرغم من الدراسات والأبحاث التي تعاملت مع استخدام مزيج الكاسر الايوني والجسيمات النانوية في تطبيقات انتاج النفط الخام، لا تتوفر بيانات دقيقة على حد علمنا عن احتمالات التأثير المتبادل والمشارك لهذا المزيج على استقرار وخواص اللزوجة لمستحلب النفط في الماء في درجات حرارة الممكن. هذه الدراسة تقدم نظرة دقيقة وتحليله للتأثير المتبادل لكواسر الشد السطحي والجسيمات النانوية على مستحلب النفط في الماء في ظروف الممكن وعمليات تحسين انتاج النفط الخام.

Introduction:

Nanotechnology implementation in enhanced oil recovery (EOR) is one of the most significant ongoing discussions in the petroleum industry. EOR is an expensive technique which applied to produce more oil once conventional waterflooding produces no more oil economically. Typically, primary and secondary (waterflooding) oil recovery can produce no more than 25 - 28% of the original oil in place (OOIP) leaving a huge amount of hydrocarbon in the pore space of the reservoir in the form of residual oil saturation. To meet the universal accelerated demand for energy, the residual oil should be produced and be part of the world's production body of oil. The recovery of residual oil, however, requires the application of advanced techniques to manipulate the in-situ rock and fluid properties via EOR methods which are also known as tertiary oil recovery. EOR methods include miscible gas (e.g. CO₂) injection, thermal, and chemical methods. The use of chemical EOR technique appears to be a suitable method to produce hydrocarbon from hard-to-produce reservoirs since the oil viscosity in such reservoirs is dramatically higher than that for conventional crude oil [1].

The emulsion is a dispersion of liquid droplets in another liquid. Keeping the liquid droplets dispersed separately in the base liquid is the key for stable emulsion. In this context, emulsifiers can provide a sufficiently enough resistance to the liquid droplets against

coalescence and creaming. Various emulsifiers including surfactant [2], polymer, colloidal particles or a combination of two different emulsifiers [3] can be used to formulate a stable emulsion [4]. Surfactant-stabilized o/w emulsions are commonly used in oil recovery [5-7]. Solid particle-stabilized emulsions, also called Pickering emulsions, have several advantages over conventional surfactant emulsions, however, they are rarely used in the oil recovery industry due to the micron size of colloidal particles [8]. Typically, due to the relatively large particles-size, trapping of these micron colloidal particles in the rock pores can dramatically reduce the porosity and permeability of oil reservoirs leading to serious issues and unfeasibility in oil recovery. Thus, reducing the initial size of colloidal particles in Pickering emulsions into sub-micron sizes (two or three orders of magnitude less than micron particles) is crucial for successful implementation of such emulsions in oil recovery.

Nanoparticles (NPs) with its particle size ranging between 1 – 100 nm (10^{-9} m) and unique surface properties are showing great potentials in oil industries including NP-stabilized emulsions (nano-emulsions). The size of nano-emulsion droplets is typically smaller than that of the pore throat which allows the droplets to pass through the pore media without significant retention [9]. Further, the viscosity of nano-emulsions is significantly higher than that of conventional emulsion [10]. This relatively high viscosity improves the mobility ratio and provides a successful method to displace heavy oil from hard-to-produce oil reservoirs. Moreover, the stability of nano-emulsions is drastically higher than that of conventional emulsion at the reservoirs harsh conditions including high temperature, pressure, and salinity [11]. Several types of NPs including silica, titanium oxide, ferric oxide, and polymers have been implemented as stabilizers solely or in a combination with the surfactant, polymers, or other different types of NPs to formulate a stable o/w or w/o Pickering emulsions [12, 13]. Silica is a very popular material in the oil industry due to its availability, low cost, and environment-friendly properties. Similarly, silica NPs is a safe, and very cheap material compare to other EOR agents such as surfactant, and polymer [14]. In this context, the efficiency of NPs as stabilizer agent depends on particles initial size, surface properties, and particle's concentration (i.e., availability of NPs at enough concentration to cover the interface of the droplet partly or entirely). Mechanistically, the adsorption of NPs onto emulsion droplets surface provides sufficient repulsive force between each two adjusted

droplets leading to a stable emulsion [15, 16]. Thus, nano-emulsions have promising potentials in EOR applications.

NPs – surfactant combination has unique properties better than that of the sole NPs or surfactant formulations. Such combination can synergistically enhance the performance of NPs and surfactant in many applications including EOR [17]. In this context, loss of surfactant molecules by adsorption into rock surface can reduce the amount of free surfactant to adsorb on the oil-water interface and thus increase the interfacial tension [18-20]. However, with the presence of NPs, the amount of loss surfactant is significantly decrease since the pore spaces will be totally or partly coated with NPs. Further, NPs can act as a carrier for surfactant via the Brownian motion of NPs into the oil/water interface [21]. Meanwhile, NPs dispersion without surfactant is critically unstable due to the rapid aggregation of NPs once it comes into contact with the liquid phase [15, 22, 23]. The rapid aggregation of NPs is related to the high surface energy of NPs as a result of the high surface to volume ratio [15]. The addition of surfactant, however, can significantly enhance the stability of NPs in the dispersion via supercharging NPs surface and thus induces the repulsive force between similarly charges NPs [24].

In the last decade, several studies have investigated the mutual effect of NPs and surfactant on the stability and rheological properties of o/w and w/o emulsions. Lan, et al. [21] investigated the formulation of stable o/w emulsion using a combination of silica NPs (200 nm) and cationic surfactant (CTAB). Their results showed that appropriate concentrations of NPs and surfactant molecules can synergistically result in very stable o/w emulsion. However, the increase in surfactant concentration can dramatically destabilize the emulsion due to the excessive desorption of NPs in the form of large aggregates from the interface. Mechanistically, the increase in cationic concentration can totally neutralize the surface charge of NPs leading to an accelerated coalescence and aggregation process of NPs [15]. At the same time and using the same types of NPs and surfactant (CTAB), Ravera, et al. [25] investigated the interfacial tension and rheological properties of hexane/water emulsion as well as the behavior of micrometric oil droplets in the emulsion. Without a deep knowledge of the mechanisms, the study showed that the NPs transfer and attachment to droplet interface are mainly governed by their surface properties and the interaction of the surfactant in the emulsion. In this context, the status of NPs at the interface varying from strongly

adsorbed to strongly desorb depending on the concentration of CTAB at the interface. In line with that, Vashisth, et al. [26] showed that adding surfactant molecules which preferentially adsorb at the oil-water interface displaces NPs effortlessly from the interface. Fan, et al. [27] using silica NPs with three different surface chemistry, revealed that the adsorption-desorption behaviour on NPs at the oil/water interface is entirely controlled by the surface properties of NPs. Typically, the surface chemistry of NPs is a function of surfactant concentration in the nanofluid [28]. Esmailzadeh, et al. [29] reported that above the critical micelle concentration (CMC, surfactant concentration above which surfactant monomers tend to form micelles) NPs have no influence on the oil-water interfacial tension. Sharma, et al. [13] formulated a stable o/w emulsion using silica NPs and sodium dodecylsulfate (SDS) as an anionic surfactant at ambient condition. Further, they formulated a thermally stable Pickering emulsion via a combination of silica NPs, SDS, and polyacrylamide (PAM) polymer at reservoir temperature and highlighted the effects of silica NPs on the efficiency of SDS, and PAM as emulsifiers [30]. Biswal, et al. [31] comprehensively studied the effect of negatively charged silica NPs on the interfacial properties of o/w emulsions at variable concentrations of four different surfactant including anionic surfactant (SDS), cationic surfactant (CTAB), and two non-ionic surfactants (Tween 20, and Triton X-100) at ambient condition. Results showed that, on the contrary of ionic surfactant, non-ionic surfactant in combination with silica NPs can increase the surface tension of the oil/water system and destabilize the emulsion. Recently, Al-Anssari and his co-researchers have investigated the practical implementation of silica NPs-SDS surfactant combination in EOR and in the associated carbon geosequestration projects [9, 15, 32-35]. Briefly, their results showed that silica NPs are inapplicable in the subsurface application without the addition of the right type and amount of surfactant. In this context, NPs can alter the wettability of oil-wet surface into water-wet via the structural disjoining pressure (SDP) of NPs. However, the activation of SDP requires in between wedge between the rock surface and oil droplet. Typically, this wedge is not available when the contact angle is higher than 90° which is mostly the case in carbonate reservoir. Thus it is essential to use another surface active material to reduce the contact angle below 90° the NPs can act to synergistically alter the wettability into strongly water-wet [32]. Moreover, the presence of NPs reduces the CMC and improves the efficiency and feasibility of surfactant in EOR projects.

Despite studies investigate the o/w emulsions and the interaction effects of surfactant and NPs on the stability, interfacial and rheological properties of emulsions, there is a serious lack of information about the correct NPs/surfactant ratios to formulate stable and efficient o/w emulsion for EOR application. This study thus presents the formulation of stable o/w emulsion augmented by silica NPs and SDS surfactant and investigates the optimum concentration of these surface-active agents to achieve a stable emulsion. Also, the range of NPs-SDS concentration that assures a synergistic effect on emulsion properties was investigated.

Materials and Methods:

Materials:

Silica NPs (white powder, 99.5 wt% SiO₂, Molecular mass of 60.08 g/mol) with initial particle size ranging between 5 – 10 nm was supplied by Sigma-Aldrich. These insoluble NPs have a specific surface area of 140 m²/g and zeta potential of -32.15 mV, according to the supplier.

Sodium dodecylsulfate (SDS, ≥98.5 mol%, Molecular mass 288.38 g/mol, CMC = 2450 mg/L) was purchased from Sigma-Aldrich. The CMC value was double-checked via electrical conductivity methods (using RS 180-7127 conductivity meter) and it was too close to the value given by the supplier with less than 0.17% percentage error. To keep consistency with our previous studies [9, 15, 32, 33, 36, 37], n-Decane (>99 mol% purity, from Sigma-Aldrich) was used as model oil to formulate o/w emulsion. Deionized (DI) water (Ultrapure from David Gray; conductivity = 0.02 mS/cm) was utilized in all experiments. Sodium Chloride (NaCl; ≥ 99.5 mol% purity) supplied by Scharlan was used to control the salinity of the aqueous phase.

All aqueous solutions were formulated utilizing a five digits analytical weighing balance ((Model BTA-623, 0.001 g, Phoenix Instruments). Further, to avoid any unfavorable increase in temperature and its potential negative impact on surfactant properties, all mixing process was conducted in two stages. Initially, with the absence of NPs, using magnetic stirrer (Across International). And then using ultrasonic homogenizer (Model 300 VT Ultrasonic

Homogenizer, Biologics) with the presence of NPs. All laboratory devices used in this study was illustrated and showed in our previous work [38].

Formulation of o/w emulsion:

In this study, o/w emulsion was formulated via dispersing of n-decane in the water phase which holding a suspension of NPs in a surfactant solution. the emulsification ratio was constant at 25:75 oil to water volume ratio [13, 14, 31]. Initially, brine at the desired concentration was prepared to be used as a water phase in the subsequent steps. Then aqueous surfactant solutions were formulated via magnetic stirring of the desired amount of surfactant solid powder with brine. Although the rpm and period of stirring are mainly depending on the composition of the aqueous phase, all samples in this study were formulated at 800 rpm for 6 hours. Subsequently, NPs were dispersed in the aqueous phase via sonication of the desired weight of NPs with the surfactant solution. Eventually, o/w emulsion was formed via the dispersion of fixed ratios of n-decane to the aqueous phase (25:75) utilizing the same ultrasonic homogenizer at the power of 240 W for 4 minutes. The cooling bath was used during the sonication process to avoid the damaging effect of increased temperature on surfactant monomers. The status of the emulsion was visually monitored and, when necessary photographed at varied periods to observe the emulsion stability. Further monitoring was conducted via droplet size and zeta potential measurements.

Emulsion Characterization:

Droplet size distribution and of o/w emulsion augmented by silica NPs and SDS anionic surfactant was measured utilizing a dynamic light scattering (DLS; Nano ZS, Malvern Instruments). The DLS is based on the Brownian motion of the suspended droplets or particles. The principle of Brownian motion is the droplets are constantly colliding with the base fluid molecules. These collisions result in a specific amount of energy to be transferred, which induce droplet motion. This energy has greater effect on smaller droplets than larger once. Thus, smaller droplets are moving at higher speed than larger droplets. Consequently, DLS can determine the hydrodynamic diameter by measuring the speed of the droplets. Also, to understand the physicochemical characteristics of the emulsion, the range of the electrostatic force between emulsion droplets was investigated via zeta potential (ζ) measurements [39]. Zetasizer (zetasiser; Nano ZS, Malvern Instruments) was used for these

measurements. In this context, ζ was obtained from the electrophoretic mobility and application of the Smoluchowski-Helmholtz equation [23]. Each experiment was repeated three times.

Rheological Measurements:

Rheological measurements were conducted using Discovery HR-3 hybrid rheometer, which equipped with temperature control. Experimentally, the effect of different parameters including SDS, and NPs concentrations in the emulsion, aging and operational conditions (time, temperature, and shear rate) on emulsion rheological properties. Further, viscosity was measured at different rotational speeds (1 – 500 rpm). The viscosity curves can be analyzed using mathematical models such as Power law (Ostwald de Waele) and Bingham plastic model [40].

Result and Discussion:

The studies on physicochemical characterization and droplet size distribution of o/w emulsion augmented by anionic surfactant and hydrophilic NPs are presented and discussed in this section.

Stability of o/w emulsion augmented by NPs-surfactant combination:

O/W emulsion stability in the presence of silica NPs/SDS surfactant was first evaluated visually using transparent bottles and then via physicochemical measurements. Visually, all the formulated emulsions were stable against creaming and/or water phase separation along the two weeks of testing. However, a slight water separation in some samples was later noticed in the second week. Monitoring of o/w phase behavior showed that at relatively high surfactant concentration (\geq CMC), the increase in NPs concentration has entirely no influence on the stability of the emulsion. While below CMC, NPs increases induce the stability of the emulsion. Thus, the NPs/SDS synergistic effect on o/w emulsion stability is limited by the concentrations below CMC. This is consistent with the reported data in the literature regarding the mutual effect of NPs-surfactant combination on oil/water interfacial tension [33]. Typically, stable o/w emulsion can be formulated when the oil/water interfacial tension is ultimately low [41]. In this context, the reduction of oil/water interfacial tension depends on the extent of surfactant adsorption on the oil/water interface. At low surfactant

concentration (\leq CMC), a limited number of monomers can reach the oil/water interface via monomer diffusion. In this case and due to the Brownian motion, NPs may act as carrier agents to increase surfactant monomers near the interface. Thus, the rate of surfactant adsorption increases leading to a significant reduction on o/w interfacial tension referring to the stable emulsion. This synergistic effect will no longer available at high surfactant concentration (\geq CMC). In this case, the high amount of surfactant monomer near the interface, due to high concentration, subsequently increases the rate of monomers adsorption and thus reduces the interfacial tension without the effect of NPs [41]. Some studies argued that at high surfactant concentration, the significant repulsive forces between similarly charged NPs and surfactant monomer can push the monomer towards the interface and that is also synergistic effect [25]. However, Al-Anssari, et al. [15] demonstrated that surfactant monomer can be attached into similarly charged NPs from the tail group.

Characterization of o/w emulsions:

Sufficient electrostatic repulsive force between o/w emulsion droplets is a key for a stable or thermodynamically stable emulsion. In this context, zeta potential (ζ) of emulsion droplets is a direct scale for such repulsive forces. Physiochemically, ζ of each droplet in the emulsion is the electrostatic potential at the electrical double layer surrounding the colloid particle or droplet in solution [39]. Characteristically, Droplets or NPs with ζ between -10 and +10 mV are considered electrostatically neutral and thus significantly unstable. While droplets with ζ of greater than +30 mV or less than -30 mV are electrostatically stable against collision and coalescence. Table.1 contains more details on ζ ranges and stability. Emulsion with ζ value lower than ± 30 mV tends to aggregate and coalesce due to the weak repulsive force between droplets.

Typically, the ionic surfactant can improve the stability of colloidal systems including o/w emulsion if correctly formulated. Thus, ζ was measured at different SDS concentrations Figure (1). In this study, the maximum test concentration of SDS was 0.5 wt%. Further increasing in SDS concentration is unfeasible in a real subsurface application for two reasons. First, these materials are complicated and expensive thus minimize the amount of injected surfactant into the subsurface formation is preferable from the environmental and economic point of view.

Table (1) Relation between stability and zeta potential values

Zeta potential range (ζ mV)	Stability condition
$\pm 0 \longrightarrow \pm 10$	Significantly instable
$\pm 10 \longrightarrow \pm 30$	Instable
$\pm 30 \longrightarrow \pm 60$	Stable
$\pm 60 \longrightarrow \pm 100$	Highly stable

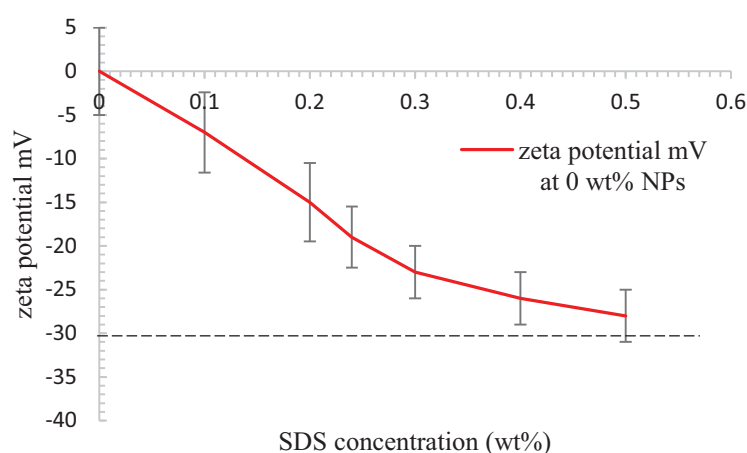


Fig. (1) Zeta potential of o/w emulsion at various anionic surfactant concentration (wt% SDS) without the addition of NPs. Black dashed line represents limits between stable and unstable regions.

Figure (1) starkly declared that even at relatively high concentration (SDS wt% \geq CMC), anionic surfactant can't thermodynamically stabilize the o/w emulsion without the addition of another agent (co-stabilizer). Mechanistically, the addition of anionic surfactant induces the charge of the emulsion in the negative direction. The increase in SDS concentration shifts the emulsion from the neutral region (significantly unstable; zeta potential ≤ -10 mV) into unstable region ($-10 \geq$ zeta potential ≥ -30 mV). Results showed that at CMC of SDS the zeta potential was around -20 mV, which still within the unstable region. Further increase in SDS concentration reaching 0.5 wt%, which is the double of CMC, can shift zeta potential to reach 28 ± 3 mV at the edge of the stable region. However, such critically stable emulsions are inapplicable for subsurface applications considering the effect of in-situ operation conditions including pressure, temperature, and salinity. This is consistent with several previous studies

that suggested the addition of another agent such as a polymer, NPs or polymer-NPs combination. Figure (2) shows the transition of emulsion status from instability region to a stable region under the effect of NPs.

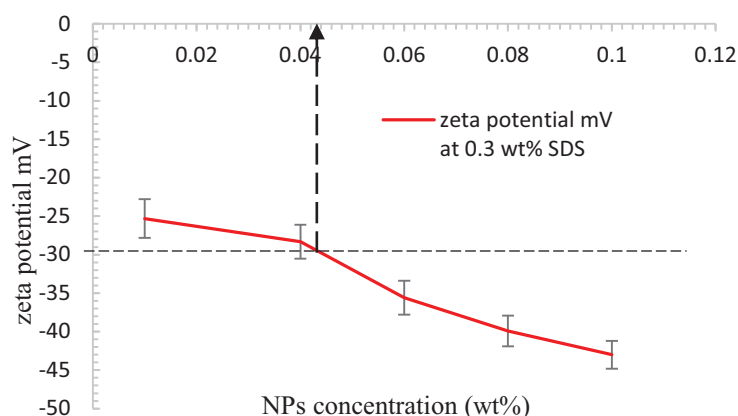


Fig. (2) Zeta potential at 0.3wt% SDS (just above the CMC) and various NPs concentration (NPs wt%)

Results showed that in the absence of NPs, zeta potential values of o/w emulsions were below the stability region (i.e. < 25 mV) although SDS concentration was higher than the CMC (i.e. 0.3 wt% SDS). Thus, surfactant by itself, even at relatively high concentration (\geq CMC), is not enough to stabilize o/w emulsion. Addition of NPs, however, can gradually induce the stability by shifting zeta potential values into stability region as NPs concentration increased. The intersection point between zeta potential curve and the starting border of stability region (dashed line) reported that when SDS is 0.3 wt% (slightly above the CMC), the addition of around 0.045 wt% NPs (considering the standard deviation of measurements) cause an inversion of the emulsion status from unstable into stable condition. These NPs concentration is the minimum amount of NPs required stabilizing o/w emulsion at specific SDS concentration (0.3 wt% SDS). Similarly, the minimum concentration of NPs to stabilize emulsion at different SDS concentration can be measured.

Droplet size and droplet size distribution of o/w emulsion:

Size and rate of size growing with a time of emulsion droplets are a clear and direct tool to evaluate the stability of the emulsion. In this section, both microscopic images Figure (3) and

dynamic light scattering (DLS) measurements Figure (4) were used to evaluate the average droplet size of o/w emulsion directly after the formulation of the emulsion and after two weeks of storage. Emulsions were stored in a cold and dark place to avoid the natural degrading effect of heat and light. In this section, despite the optimum values of SDS, and NPs concentration for stable o/w emulsion, low NPs concentration (≤ 0.03 wt% NPs dispersed in SDS solution) was used in this test to avoid the opaque nature of concentrated silica nanofluids. Typically, DLS is a laser-based technique. Measurements using such laser-based devices require a transparent or at least not opaque samples to provide accurate measurements [15]. Microscopic images showed that droplets morphology remained nearly unchanged along the storage period of 14 days. This observation was consistent with droplet size distribution and average droplet size measurement of the same samples Figure (4).

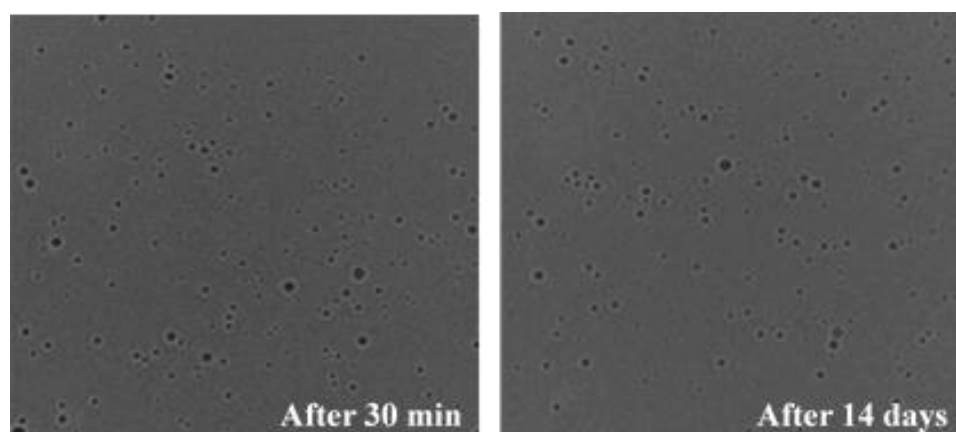


Fig. (3) Microscopic images for emulsion droplets size maps after two different periods of time from the formulation.

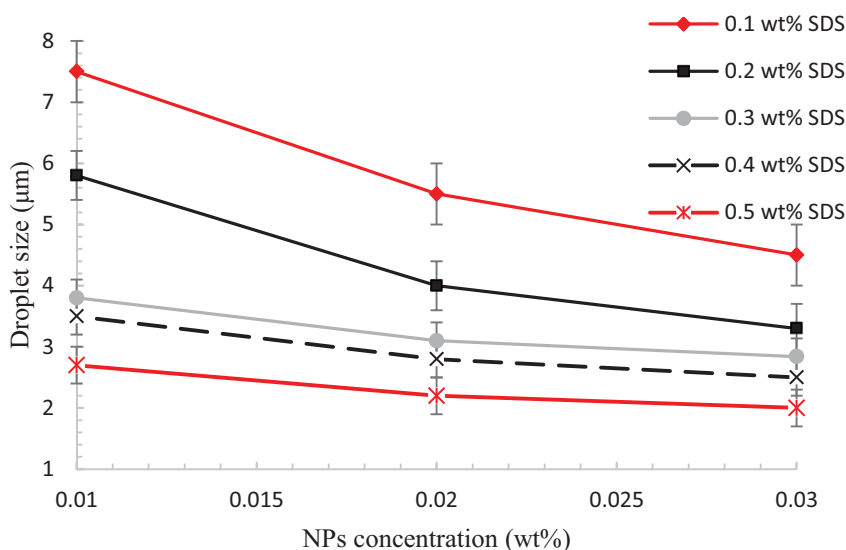


Fig. (4) Average droplet size of o/w emulsion at various NPs (0.01 – 0.03 wt%) and SDS (0.1 – 0.5 wt%) concentrations after 30 min from preparation at ambient conditions.

Results reported that the average droplet size after 30 min was 2480 nm (2.48 µm) while the average droplet size measured after 14 days was 3080 nm (3.08 µm) referring to the only slight growing of particle size. Mechanistically, the co-existence of NPs -SDS combination creates a kind of production mono or multi-layer shield around the droplet. This surface-active shield prevents droplets collision and coalescence and keeps the droplet solely suspended in the emulsion. Typically, using higher NPs concentration can enhance the stability of o/w emulsion via narrowing the droplet size at smaller average droplet size.

Impact of temperature and salinity on rheological properties of NPs-SDS stabilized emulsions:

The effect of NPs-SDS combination on the rheological properties of o/w emulsion has presented with details in several published papers. However, reservoir conditions including temperature and salinity on the rheological properties of these NPs-SDS augmented emulsion have poorly investigated. This section thus examined the effect of increased temperature (23 - 70°C) and electrolyte strength (0 – 5 wt% NaCl) on the viscosity of o/w silica NPs-SDS surfactant-stabilized emulsion at a constant shear rate Figure (5).

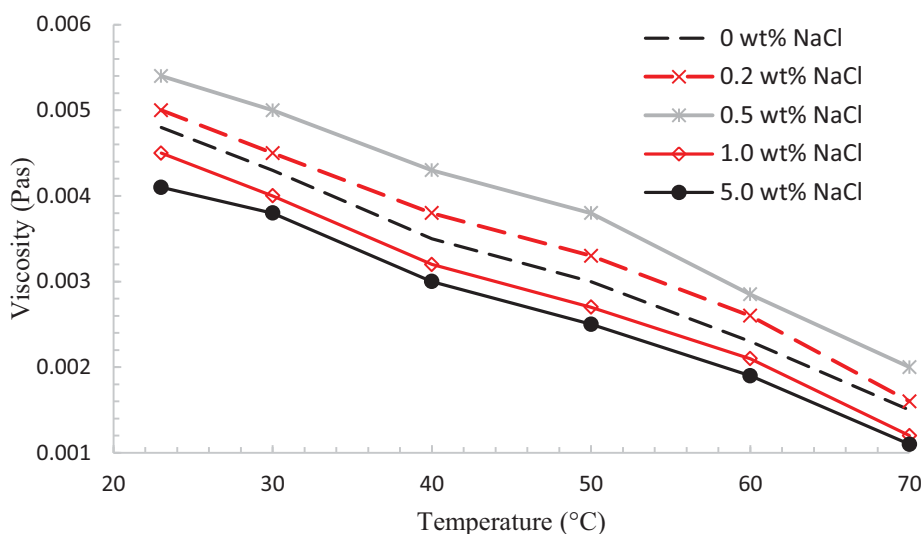


Fig. (5) Effect of temperature and salinity on the viscosity of o/w emulsion stabilized by NPs (0.03 wt%) - SDS (0.3 wt%) solution at a constant share rate of 5 s^{-1} .

Results showed that increased temperature reduces the viscosity of the emulsion which is consistent with reported data regarding all type of emulsions including pickling o/w emulsions. Typically, viscosity reduction with increased temperature is mainly related to the effect of the head on the continuous phase of the emulsion. Further, flocculation of the dispersed phase at higher temperatures, mainly due to higher surfactant solubility at a higher temperature, can induce the reduction in viscosity [10, 13].

On the other hand, salinity has shown more complicated influences on emulsion viscosity. Results showed that at relatively low salinity (0 – 0.2 wt% NaCl), no significant effect was noticed on the viscosity at all temperatures. Further increase in salinity (0.5 wt% NaCl) can increase the viscosity more significantly. While salinity increasing into higher NaCl concentration reduce the viscosity again to a value lower than that recorded with DI-water. Specifically, at high salinity, the more salt is added the less viscosity is recorded. The complex behavior of emulsion viscosity at elevated salinity is related to several factors such as the effect of salinity on the CMC and solubility of surfactant molecules as well as the wettability of NPs surfaces which controls the adsorption of these NPs onto the oil/liquid interface [33].

Conclusion:

The stability and rheological property of decane/water oil-in-water emulsion which stabilized by silica nanoparticles (NPs)-SDS anionic surfactant were investigated to assess the efficiency NPs/SDS combination in enhanced oil recovery (EOR) projects. Results from extensive zeta potential (ζ) and droplet size distribution indicate the high potential of this combination as an emulsion stabilizer. Addition of NPs-SDS combination can shift ζ of the emulsion into the stable region (≥ 30 mV) via inducing the negativity of the aqueous phase. In this context, attachment of anionic surfactant via its tail group into similarly charged hydrophilic silica NPs can supercharge the colloid particles [24]. These supercharged NPs by SDS monomers is a superior emulsion stabilizer [10]. Further, viscosity measurements at different temperature and salinities reveal the extent of NPs-SDS combination coherent at reservoir condition. Further, considering the environmental and economic requirements in subsurface projects, the optimum concentrations of silica NPs and SDS for efficient o/w emulsion was measured and specified. Thus, NPs can synergistically stabilize o/w emulsion if correctly formulated with SDS anionic surfactant.

References:

1. H. Pei, G. Zhang, J. Ge, M. Tang, Y. Zheng, Comparative effectiveness of alkaline flooding and alkaline–surfactant flooding for improved heavy-oil recovery, *Energy & Fuels* 26(5) (2012) 2911-2919.
2. S. Iglauer, Y. Wu, P. Shuler, Y. Tang, W.A. Goddard Iii, New surfactant classes for enhanced oil recovery and their tertiary oil recovery potential, *Journal of Petroleum Science and Engineering* 71(1–2) (2010) 23-29.
3. S.K. Rai, A. Bera, A. Mandal, Modeling of surfactant and surfactant–polymer flooding for enhanced oil recovery using STARS (CMG) software, *J Petrol Explor Prod Technol* 5(1) (2015) 1-11.
4. A. Nesterenko, A. Drelich, H. Lu, D. Clause, I. Pezron, Influence of a mixed particle/surfactant emulsifier system on water-in-oil emulsion stability, *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 457 (2014) 49-57.
5. A.J. Worthen, S.L. Bryant, C. Huh, K.P. Johnston, Carbon dioxide-in-water foams stabilized with nanoparticles and surfactant acting in synergy, *AIChE Journal* 59(9) (2013) 3490-3501.
6. A.J. Worthen, L.M. Foster, J. Dong, J.A. Bollinger, A.H. Peterman, L.E. Pastora, S.L. Bryant, T.M. Truskett, C.W. Bielawski, K.P. Johnston, Synergistic Formation and Stabilization of Oil-in-Water Emulsions by a Weakly Interacting Mixture of Zwitterionic Surfactant and Silica Nanoparticles, *Langmuir* 30(4) (2014) 984-994.
7. A.J. Worthen, P.S. Parikh, Y. Chen, S.L. Bryant, C. Huh, K.P. Johnston, Carbon dioxide-in-water foams stabilized with a mixture of nanoparticles and surfactant for CO₂ storage and utilization applications, *Energy Procedia* 63 (2014) 7929-7938.
8. T. Zhang, D. Davidson, S.L. Bryant, C. Huh, Nanoparticle-Stabilized Emulsions for Applications in Enhanced Oil Recovery, *Improved Oil Recovery*, Society of Petroleum Engineers, Tulsa, Oklahoma, USA, 2010.
9. S. Al-Anssari, L.N. Nwideo, M. Ali, J.S. Sangwai, S. Wang, A. Barifcani, S. Iglauer, Retention of Silica Nanoparticles in Limestone Porous Media, *SPE/IATMI Asia Pacific Oil & Gas Conference and Exhibition*, 17-19 October , Jakarta, Indonesia, Society of Petroleum Engineers, 2017.

10. N.K. Maurya, A. Mandal, Investigation of synergistic effect of nanoparticle and surfactant in macro emulsion based EOR application in oil reservoirs, *Chemical Engineering Research and Design* 132 (2018) 370-384.
11. H. ShamsiJazeyi, C.A. Miller, M.S. Wong, J.M. Tour, R. Verduzco, Polymer-coated nanoparticles for enhanced oil recovery, *Journal of Applied Polymer Science* 131(15) (2014) 1-13.
12. M. Shen, D.E. Resasco, Emulsions Stabilized by Carbon Nanotube–Silica Nanohybrids, *Langmuir* 25(18) (2009) 10843-10851.
13. T. Sharma, G.S. Kumar, B.H. Chon, J.S. Sangwai, Thermal stability of oil-in-water Pickering emulsion in the presence of nanoparticle, surfactant, and polymer, *Journal of Industrial and Engineering Chemistry* 22 (2015) 324-334.
14. T. Sharma, G. Suresh Kumar, J.S. Sangwai, Enhanced oil recovery using oil-in-water (o/w) emulsion stabilized by nanoparticle, surfactant and polymer in the presence of NaCl, *Geosystem Engineering* 17(3) (2014) 195-205.
15. S. Al-Anssari, M. Arif, S. Wang, A. Barifcani, S. Iglauer, Stabilising nanofluids in saline environments, *Journal of Colloid and Interface Science* 508 (2017) 222-229.
16. M. Luo, Y. Song, L.L. Dai, Heterogeneous or competitive self-assembly of surfactants and nanoparticles at liquid–liquid interfaces, *Molecular Simulation* 35(10-11) (2009) 773-784.
17. M.A. Ahmadi, S.R. Shadizadeh, Induced effect of adding nano silica on adsorption of a natural surfactant onto sandstone rock: Experimental and theoretical study, *Journal of Petroleum Science and Engineering* 112 (2013) 239-247.
18. K. Ma, L. Cui, Y. Dong, T. Wang, C. Da, G.J. Hirasaki, S.L. Biswal, Adsorption of cationic and anionic surfactants on natural and synthetic carbonate materials, *Journal of Colloid and Interface Science* 408 (2013) 164-172.
19. T. Amirianshoja, R. Junin, A. Kamal Idris, O. Rahmani, A comparative study of surfactant adsorption by clay minerals, *Journal of Petroleum Science and Engineering* 101 (2013) 21-27.
20. A. Bera, T. Kumar, K. Ojha, A. Mandal, Adsorption of surfactants on sand surface in enhanced oil recovery: Isotherms, kinetics and thermodynamic studies, *Applied Surface Science* 284 (2013) 87-99.

21. Q. Lan, F. Yang, S. Zhang, S. Liu, J. Xu, D. Sun, Synergistic effect of silica nanoparticle and cetyltrimethyl ammonium bromide on the stabilization of O/W emulsions, *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 302(1–3) (2007) 126-135.
22. A. Amiri, G. Øye, J. Sjöblom, Influence of pH, high salinity and particle concentration on stability and rheological properties of aqueous suspensions of fumed silica, *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 349(1–3) (2009) 43-54.
23. S. Al-Anssari, S. Wang, A. Barifcani, M. Lebedev, S. Iglauer, Effect of temperature and SiO₂ nanoparticle size on wettability alteration of oil-wet calcite, *Fuel* 206 (2017) 34-42.
24. S. Ahualli, G.R. Iglesias, W. Wachter, M. Dulle, D. Minami, O. Glatter, Adsorption of Anionic and Cationic Surfactants on Anionic Colloids: Supercharging and Destabilization, *Langmuir* 27(15) (2011) 9182-9192.
25. F. Ravera, M. Ferrari, L. Liggieri, G. Loglio, E. Santini, A. Zanobini, Liquid–liquid interfacial properties of mixed nanoparticle–surfactant systems, *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 323(1–3) (2008) 99-108.
26. C. Vashisth, C.P. Whitby, D. Fornasiero, J. Ralston, Interfacial displacement of nanoparticles by surfactant molecules in emulsions, *Journal of Colloid and Interface Science* 349(2) (2010) 537-543.
27. H. Fan, D.E. Resasco, A. Striolo, Amphiphilic Silica Nanoparticles at the Decane–Water Interface: Insights from Atomistic Simulations, *Langmuir* 27(9) (2011) 5264-5274.
28. M.A. Ahmadi, S.R. Shadizadeh, Adsorption of Novel Nonionic Surfactant and Particles Mixture in Carbonates: Enhanced Oil Recovery Implication, *Energy & Fuels* 26(8) (2012) 4655-4663.
29. P. Esmailzadeh, N. Hosseinpour, A. Bahramian, Z. Fakhroueian, S. Arya, Effect of ZrO₂ nanoparticles on the interfacial behavior of surfactant solutions at air–water and n-heptane–water interfaces, *Fluid Phase Equilibria* 361(0) (2014) 289-295.
30. T. Sharma, G.S. Kumar, J.S. Sangwai, Comparative effectiveness of production performance of Pickering emulsion stabilized by nanoparticle–surfactant–

- polymerover surfactant–polymer (SP) flooding for enhanced oil recoveryfor Brownfield reservoir, *Journal of Petroleum Science and Engineering* 129 (2015) 221-232.
31. N.R. Biswal, N. Rangera, J.K. Singh, Effect of Different Surfactants on the Interfacial Behavior of the n-Hexane–Water System in the Presence of Silica Nanoparticles, *The Journal of Physical Chemistry B* 120(29) (2016) 7265-7274.
 32. S. Al-Anssari, L.N. Nwidee, M. Arif, S. Wang, A. Barifcani, M. Lebedev, S. Iglauer, Wettability Alteration of Carbonate Rocks via Nanoparticle-Anionic Surfactant Flooding at Reservoirs Conditions, *SPE Symposium: Production Enhancement and Cost Optimisation*, Society of Petroleum Engineers, 7-8 November, Kuala Lumpur, Malaysia, 2017.
 33. S. Al-Anssari, S. Wang, A. Barifcani, S. Iglauer, Oil-water interfacial tensions of silica nanoparticle-surfactant formulations, *Tenside Surfactants Detergents* 54(4) (2017) 334-341.
 34. S. Al-Anssari, Z.-U.L.A. Arain, A. Barifcani, A. Keshavarz, M. Ali, S. Iglauer, Influence of Pressure and Temperature on CO₂-Nanofluid Interfacial Tension: Implication for Enhanced Oil Recovery and Carbon Geosequestration, *Abu Dhabi International Petroleum Exhibition & Conference*, Society of Petroleum Engineers, Abu Dhabi, UAE, 2018, p. 11.
 35. S. Al-Anssari, A. Barifcani, A. Keshavarz, S. Iglauer, Impact of nanoparticles on the CO₂-brine interfacial tension at high pressure and temperature, *Journal of Colloid and Interface Science* 532 (2018) 136-142.
 36. S. Al-Anssari, A. Barifcani, S. Wang, M. Lebedev, S. Iglauer, Wettability alteration of oil-wet carbonate by silica nanofluid, *Journal of Colloid and Interface Science* 461 (2016) 435-442.
 37. S. Al-Anssari, M. Arif, S. wang, A. Barifcani, L. Maxim, S. Iglauer, Wettability of nanofluid-modified oil-wet calcite at reservoir conditions, *Fuel* 211 (2018) 405-414.
 38. S. Al-Anssari, *Application of Nanotechnology in Chemical Enhanced Oil Recovery and*
 39. *Carbon Storage*, Department of Chemical Engineering, Curtin University, 2018, p. 244.

40. J.D. Clogston, A.K. Patri, Zeta Potential Measurement, in: S.E. McNeil (Ed.), Characterization of Nanoparticles Intended for Drug Delivery, Humana Press, Totowa, NJ, 2011, pp. 63-70.
41. N. Kumar, A. Mandal, Oil-in-water nanoemulsion stabilized by polymeric surfactant: Characterization and properties evaluation for enhanced oil recovery, European Polymer Journal 109 (2018) 265-276.
42. T.N. Castro Dantas, P.J. Soares A, A.O. Wanderley Neto, A.A. Dantas Neto, E.L. Barros Neto, Implementing New Microemulsion Systems in Wettability Inversion and Oil Recovery from Carbonate Reservoirs, Energy & Fuels 28(11) (2014) 6749-6759.