

Low Salinity Surfactant Flooding: Role of Surfactant and Salt



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Abstract The need for effective enhanced oil recovery (EOR) methods in terms of economics and technical feasibility are growing rapidly along with the steeply growing demand for crude oil in the energy sector. Such demands driving researchers to innovate novel EOR solutions and also to explore ways to enhance the effectiveness of conventional EOR methods. This chapter summarises advancement in one such hybrid EOR method developed by combining novel low salinity water flooding with conventional surfactant flooding. The synergistic benefits of low salinity water and different low salinity surfactant formulations in terms of improving reservoir properties and oil recovery efficiency are summarized. This chapter also aims to provide a very detailed discussion on the complex pore level mechanism of oil recovery through the hybrid low salinity surfactant flooding process.

1 Introduction

Surfactant flooding is one of the oldest and the most widely used chemical enhanced oil recovery (EOR) method practiced by the oil industry. It involves the injection of an aqueous solution of surfactant into oil reservoirs generally tailored with water flooding. A surfactant solution in the reservoirs can produce ultra-low oil–water interfacial tension, increase the capillary number to a great extent, causes water wetness of the reservoir rock and in-situ emulsification of oil and water which enhances pore level displacement efficiency of the crude oil [1, 2]. Surfactant flooding, although it has distinctive working mechanisms, it is generally applied in combination with other chemical EOR methods like polymer flooding and alkaline flooding [3].

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T. Solling et al. (eds.), *Surfactants in Upstream E&P*, Petroleum Engineering, https://doi.org/10.1007/978-3-030-70026-3_8

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Synergism between different EOR methods is always served as an optimization route for maximizing oil recovery and reducing the cost of EOR operations. One such novel EOR method whose synergism has been studied with other chemical EOR methods in recent times is the 'low salinity water flooding'. This method is based on designing of the injection water chemistry, ideally one with injection water salinity much lower than that of the reservoir connate water [4, 5]. The method is found to be effective in increasing oil recovery from the laboratory as well pilot scale applications [6–12] however, it is also proven to be an excellent partner in producing synergistic benefits with other chemical EOR methods. Many laboratory investigations have shown that low salinity water flooding, when applied in combination, can be effective in enhancing oil recovery as well as in mitigation of many problems that arise during chemical EOR such as polymer flooding and surfactant flooding [13–16]. The synergistic benefits of low salinity water flooding with chemical EOR methods lead to hybrid EOR concepts such as low salinity surfactant flooding and low salinity polymer flooding.

This chapter summarizes the development in the field of low salinity surfactant flooding including the effect of low salinity surfactant formulation on reservoir properties, their oil recovery efficiency obtained from laboratory studies and the pore level physicochemical mechanism involved.

2 Low Salinity Water Flooding

The petrophysics and surface chemistry research group at the University of Wyoming while studying wettability effects on waterflooding observed that change in injection brine salinity affects oil recovery [17]. Advancement of their research on the impact of brine salinity on oil recovery established that reducing injection brine salinity can increase oil recovery by waterflooding [11, 18, 19]. Their research was actively followed by researchers of British Petroleum through numerous laboratory and single-well tests which finally led to the registration of LoSal™ [7, 12, 20, 21]. Meanwhile, researchers from industry and academia actively participated in investigating the low salinity waterflooding process. Most of the laboratory core flooding investigation showed positive results whereas a few reported no incremental recoveries. Apart from laboratory evaluations, low salinity water flooding has been tested in pilot-scale in many parts of the world e.g. Alaska, North Sea, Wyoming, Syria, and Kuwait, etc. [7, 9, 10, 12, 21, 22, 23]. The majority of the projects showed significant potential for low salinity water flooding. The incremental oil recovery of low salinity water flooding from laboratory core flooding test was as high as 36% of OOIP whereas pilot-scale tests showed the maximum incremental recovery is 15% [7]. The difference in magnitude of incremental recovery arises due to the fact that, many pore volumes of low salinity water were injected in laboratory experiments which is not realistic in field applications.

Apart from investigating the efficiency of the low salinity waterflooding process another effort made by the researcher community is to understand the underlying

working mechanism. Various mechanisms of low salinity waterflooding have been identified which are: (1) formation fine migration; (2) in-situ soap generation; (3) multi-component ion-exchange; (4) mineral dissolution; (5) salting-in effect; (5) electrical double layer expansion and (6) mineral dissolution. Although different mechanisms have been identified, extensive active research is going on for the search for mechanism of the low salinity water flooding [4, 24, 25, 26]. Table 1 summarizes the proposed low salinity mechanisms. All the proposed mechanisms may not work together for every reservoir, as it may primarily depends on specific reservoir conditions.

Laboratory investigations have demonstrated that the low salinity effect is significant when certain conditions pre-exists in the reservoir. This prerequisite conditions include: (1) presence of non-swelling clay in the reservoir, (2) presence of polar component in crude oil, (3) presence of high salinity connate water in the reservoir, (4) high divalent ion concentration in the formation water, (5) significant salinity contrast between injection water and formation water [4, 5, 11]. However, some studies reported the low salinity effect even outside the regime of above conditions.

Table 1 Description of low salinity water flooding mechanisms

Low salinity mechanism	Description	Source
Fine migration	<ul style="list-style-type: none"> • Mixed wet formation fine detached from pore surface due to double layer expansion • Oil droplet adsorbed on clay fine also stripped away along with formation fine 	[11]
In-situ soap generation	<ul style="list-style-type: none"> • Low salinity water increases reservoir pH • Elevated pH causes in-situ soap generation by alkaline reactive components of crude oil 	[7]
Multi-component ion exchange	<ul style="list-style-type: none"> • Exchange of divalent cations between low salinity water and organo-metallic complexes • Resulted in decomplexation of organo-metallic complexes adsorbed on the rock surface • Wettability alteration due to desorption of organic matter 	[27]
Salting-in effect	<ul style="list-style-type: none"> • The solubility of organic material increases drastically as the salinity decreases • Adsorbed organic molecules of crude oil on the clay surface detached and dissolves into water • Desorption of organic material increases water-wetness of the reservoirs rock 	[28]
Double layer expansion	<ul style="list-style-type: none"> • Increasing electrostatic repulsion of between crude oil and sandstone surface • Expansion of intervening water film 	[29]
Mineral dissolution	<ul style="list-style-type: none"> • Dissolution of carbonate minerals like anhydrite, dolomite or calcite and release of particle • Increase in pressure and wettability alteration promote oil recovery 	[30]

3 Low Salinity Surfactant Flooding

The role of salinity and salinity gradient on the surfactant flood process has been a topic of interest for many petroleum researchers since many decades. A salinity gradient implies formation or waterflood brine more saline than surfactant slug and surfactant slug more saline than the chase brine. Some studies reported a negative impact of salinity gradient on surfactant flooding in terms of minimizing ion-exchange and maintaining optimal salinity in the mixing zone [31, 32]. On the other hand, there are studies which claimed that a salinity gradient can result in higher oil recovery efficiency as compared to constant salinity [33, 34]. A salinity gradient is also observed to be responsible for lowering surfactant adsorption to nearly half as compared to constant salinity [34, 35]. The salinity level is known to control the phase behavior of a surfactant/oil/brine system as: (1) low salinity results in type II (-) or under-optimum emulsion where surfactant predominantly partitions into aqueous phase; (2) high salinity results in type II (+) or over-optimum emulsion where surfactant predominantly partitions into oleic phase; (3) optimal salinity resulted in type (III) or middle phase emulsion which causes lowest interfacial tension value as shown in Fig. 1. An increase in salinity shows a steady progression from type II (-) through type (III) to type II (+) phase behavior [36].

In the present time the growing interest of oil companies over low salinity water flooding has driven some researchers to explore the synergistic advantages of combining low salinity water flooding with surfactant flooding in the direction of conceptualizing a hybrid EOR method. Alagic and Skauge [37] were the first to

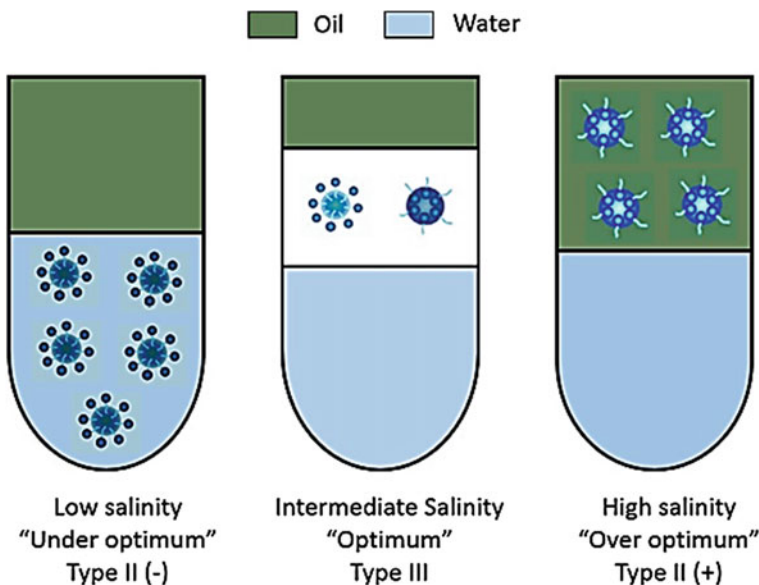


Fig. 1 Variation in types of emulsion phase behavior with salinity

investigate this low salinity surfactant synergism through a series of laboratory core flooding experiments. They observed a higher tertiary oil recovery when applied a pre-flush with low salinity brine and lower oil recovery without low salinity preflush. Meanwhile, others contributed to low salinity surfactant flooding research by investigating the rock-fluid interaction in the presence of low salinity surfactant solution in the reservoir. The low salinity surfactant flooding studies have been performed for various formulation using different surfactants like sodium dodecylbenzene sulfonate (SDBS), sodium dioctylsulfosuccinate (Aerosol OT or AOT), etc. Some of these low salinity surfactant formulations were found to have a significant impact in altering reservoir properties which could greatly favor in mobilizing residual oil. The LSS could be applied in two ways: (1) using low salinity water flooding as preflush or (2) optimal salinity surfactant injection [38].

4 Synergistic Effects of Low Salinity and Surfactant on Reservoir Properties

The most important property which has been targeted to change in surfactant EOR is the crude oil–water interfacial tension. Surfactants are capable of reducing the oil–water interfacial tension [39, 40]. A low interfacial tension between crude oil and injected water resulted in higher capillary number and formation of micro-emulsion which facilitate mobilization of entrapped residual oil. Micro-emulsions are thermodynamically stable solutions of swollen micelles and thus its formation helps in the transportation of mobilized oil in the reservoir. The relation between interfacial tension and micro-emulsion formation can be related through Eq. (1).

$$\gamma = k \left(\frac{V_{surf}}{V_{diss}} \right)^2 \quad (1)$$

where, ‘ γ ’ is the oil–water interfacial tension, ‘ V_{surf} ’ and ‘ V_{diss} ’ are the volumes of surfactant and dispersed phase (either oil or water depending on emulsion phase behavior) and ‘ k ’ is a constant whose value depends on the surfactant [41]. Thus, the interfacial tension depends on the solubilization capacity of the surfactant between oil and water. The interfacial tension reaches its minimum value when the solubilization ratio approaches unity. Generally, co-surfactants (e.g., long-chain alcohol) are added to increase the solubilization capacity of a surfactant in a micro-emulsion system and results in an ultra-low interfacial tension ($\sim 10^{-3}$ mN/m). The addition of a co-surfactant disturbs the organization of surfactant molecules at the oil–water interface which otherwise increases the stiffness of the interface [42, 43].

Recent studies of low salinity surfactant flooding show that an ultra-low interfacial tension could be achieved between crude oil and aqueous low salinity surfactant solutions without the addition of a co-surfactant [44, 45]. The interfacial tension of a pure hydrocarbon-aqueous surfactant system varies with the ionic strength of

the surfactant solution over a pH range of 2 to 10. At low pH, a high ionic strength results in higher interfacial tension; but a high pH and a low ionic strength together can increase interfacial tension of hydrocarbon-aqueous surfactant system. The presence of inorganic divalent cation in the system governs the interfacial tension behavior over varying pH range as well as the absolute value of interfacial tension (Fig. 2). With ionic surfactant in the system even at the same ionic strength, the presence of divalent cations (e.g. Ca^{2+}) can result in a significantly lowers interfacial tension. Particularly, when anionic surfactants are used, the presence of divalent ions in the solution could drop the interfacial tension to a very low value (<0.1 mN/m) [45].

When Tichelkamp et al. [45] extended their measurements of interfacial tension for crude oil-low salinity surfactant systems it was observed that the interfacial tension could reach an ultra-low value when an anionic surfactant is applied with or without divalent cations. However, depending on the nature of the crude oil the presence and absence of cations could play a role. When AOT surfactant is applied a low salinity surfactant solution can reduce the oil–water interfacial tension which could be further reduced by introducing divalent cations into the system irrespective of the crude oil type. However, the low salinity SDBS solution doesn't produce an ultra-low interfacial tension (Fig. 3).

Jha et al. [44] studied the salinity effect on interfacial tension for heptane-aqueous surfactant systems containing SDS and AOT surfactants over a wide range of salinity with varying surfactant concentrations. In-line with the earlier discussed study this

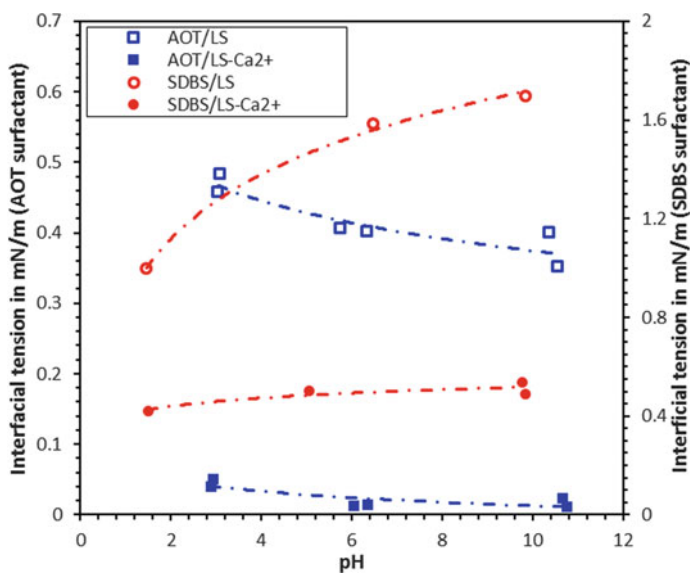


Fig. 2 The interfacial tension between a model oil (heptane + toluene in v/v: 1/1) and two anionic surfactants (SDBS and AOT) solutions as a function of pH (LS stands for low salinity water and LS-Ca²⁺ stands for low salinity water with calcium, in each case ionic strength = 20). (“Adapted with permission from [45]. Copyright 2014 American chemical society”)

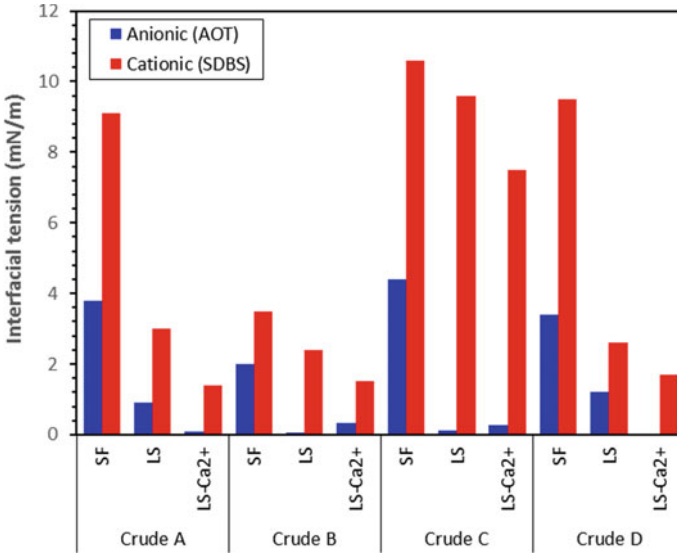


Fig. 3 Interfacial tension between crude oil and aqueous surfactant solutions of two anionic surfactants (SDBS and AOT) with no electrolyte (FS), low salinity water (LS) and low salinity water with calcium ions (LS-Ca²⁺). For crude A [°API, TAN, TBN] = [33.4, 1.08, 1.16], crude B [°API, TAN, TBN] = [34.5, 0.1, 0.56], crude C [°API, TAN, TBN] = [27.3, 2.46, -] and crude D [°API, TAN, TBN] = [44.3, 0.1, 0.18]. (“Adapted with permission from [45]. Copyright 2014 American chemical society”)

study also reported that the addition of salt can increase the ability of a surfactant to reduce the oil–water interfacial tension. However, there is an optimum salinity level for each low salinity-surfactant formulation for achieving a minimum interfacial tension value for an oil–water system. The lowest interfacial tension can be achieved when a combination of a divalent salt and anionic surfactant AOT was used. The relative concentration of divalent and monovalent ions on the interfacial tension has studied by Khanamiri et al. [46]. The optimum ionic strength corresponding to minimum IFT for crude oil-low salinity surfactant system decreases as the divalent to monovalent ratio increases. However, an increase in the relative concentration divalent doesn’t consistently result in reduced IFT, instead, there is an optimum value that exists for divalent to monovalent ration to obtain the minimum achievable IFT.

A regression model to predict the change in interfacial tension with varying salinity for a hydrocarbon-aqueous surfactant system has been proposed by Jha et al. [44] given in Eq. (2).

$$\Delta\gamma = -RTaN_S^{\max} \left(\frac{v_- + v_+}{v_-} \right) \ln \left(1 + \frac{1}{55.5M \times e^{(\Delta G_{ads}/RT)}} C_{v_-} \right) \quad (2)$$

where, ' $\Delta \gamma$ ' is the difference in interfacial tension value between the hydrocarbon-low salinity aqueous surfactant solution to that of hydrocarbon-water systems, ' R ' is the universal gas constant, ' T ' is the temperature, ' ν_- ' and ' ν_+ ' are the stoichiometric number of anions in the surfactant, ' C ' is the bulk surfactant concentration. The model has three adjustable parameters: ' a ', ' N_s^{max} ' and ' ΔG_{ads} ' represents a component specific parameter, maximum surface excess and Gibbs free energy of adsorption obtained from non-linear regression. The values of these parameters for different low salinity surfactant formulations were reported by [44].

The interfacial tension of an oil–water system in presence of surfactant depends on the aggregation behavior of the surfactant molecules at the interface of the two phases. The interfacial tension varies with the concentration of surfactant until a particular concentration level, known as critical micellar concentration (CMC). Above this concentration, the surfactant molecules start the formation of micelles and interfacial tension remains constant even with the addition of more surfactant [47]. The ionic strength of the surfactant solution governs the value of CMC. Generally, lower ionic strength results in a higher CMC value. Therefore, a low salinity surfactant solution results in lower oil–water interfacial tension as it increases the CMC value and delays the micellization process. The surfactant molecules can form different types of aggregates depending on their structure and the type of aggregation governs the value of interfacial tension. The critical packing parameter (CPP) is a number that relates the structure of the surfactant to the shape of the aggregate it forms as given in Eq. (3). [48, 49].

$$CPP = \frac{v_o}{a_e l_o} \quad (3)$$

where, ' v_o ' is the volume of the surfactant tail, ' a_e ' is the equilibrium area per molecule at the aggregate interface and ' l_o ' is the length of the surfactant tail. The values of CPP for the formation of a spherical, cylindrical, bilayer, and inverted structure are $CPP \leq 1/3$, $1/3 \leq CPP \leq 1/2$, $1/2 \leq CPP \leq 1$, $CPP \geq 1$, respectively [49, 50]. When the CPP approaches unity, the surfactant molecules aggregates to form a lamellar structure where the surfactant molecules form tight packing leads to a minimum interfacial tension value. For common surfactants, the v_o/l_o value is constant and thus only reflects the specificity of surfactant in the CPP [48]. In case of an ionic surfactant addition of salt into the system causes charge shielding and resulted in a decrease of the surfactant head group area. Small head group area helps in the formation of bilayer aggregates [44, 45]. This effect is maximum observable at an optimal salt concentration whereby the interfacial tension is minimum. Again, another important factor that governs the shape of surfactant aggregates is the 'surfactant aggregation number' which can be defined as the number of surfactant molecules in a micelle above CMC. A decrease in ionic strength results in a decrease in the aggregation number. Again, a decrease in the aggregation number changes the shape of the micelles from spherical to bilayer [48]. Studies also showed that the divalent cations particularly calcium forms stronger binding with anionic surfactants

and leads to extra tight packing at the interface [51]. The lower interfacial tension values with AOT surfactant is the result of higher CPP due to its two-tailed structure in comparison to one-tailed SDBS.

Wetting is another important property that plays a vital role in the oil displacement process during chemical EOR applications. A detailed study on the effect of salinity on wetting of reservoirs rock during surfactant flooding is not reported in the literature. However, there are few studies available which partly studied this effect through oil desorption and contact angle measurements for a very limited number of low salinity surfactant formulations [46, 52].

Figure 4 portrays oil desorption efficiencies of low salinity surfactant formulations from silica and an Al–silicate coated quartz surface. The silica surface represents sandstone and the Al–silicate simulates clay mineral often present in sandstone reservoirs. The oil desorption efficiency increases with an increase in surfactant concentration for both surfaces. The low salinity surfactant solutions of both AOT and SDBS surfactant increases the oil desorption from the mineral surfaces. The AOT showed higher potential for oil desorption compared to the SDBS surfactant. Apart from salinity and surfactant type, the oil desorption depends also on the mineral that constitutes the rock surface. The desorption was much higher for the silica surface in comparison to the Al–silicate surface [52].

Khanamiri et al. [46] studied the efficiency of low salinity surfactant formulations with a varying range of monovalent to the divalent ratio in altering wettability of a mineral surface through contact angle measurements. An alkylbenzene sulfonate

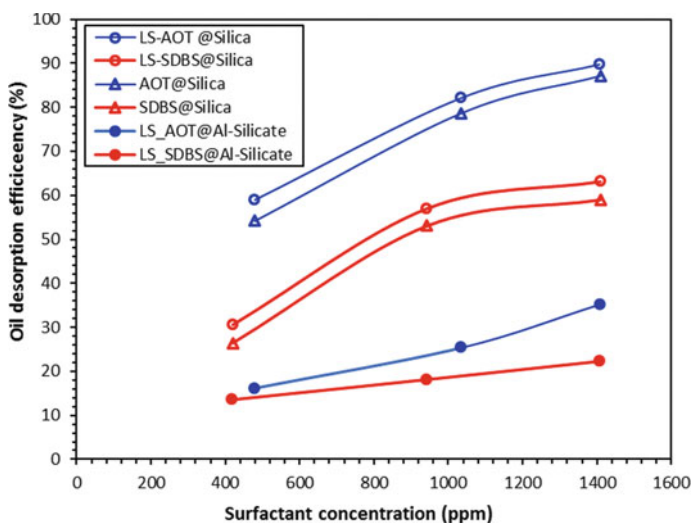


Fig. 4 Oil desorption efficiency from silica and Al–silicate surfaces as a function of surfactant concentration for different low salinity surfactant and surfactant formulation with AOT and SDBS surfactants obtained from quartz crystal microbalance (QCM) measurements. (“Adapted with permission from Nourani [52]. Copyright 2014 American chemical society”)

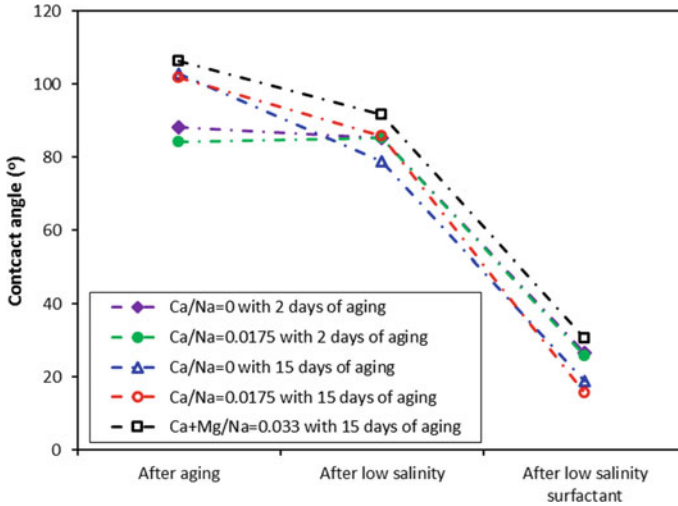


Fig. 5 Contact angles on a silicon dioxide coated crystal of an alkylbenzenesulfonate surfactant (chain length distribution of C_{15} – C_{18}) solution droplet before and treatment in low salinity surfactant. (“Adapted with permission from Khanamiri et al. [46]. Copyright 2016 American chemical society”)

surfactant with chain length distribution of C_{15} – C_{18} was used at a concentration of 21.5 weight %. The measured contact angles of the deionized water droplets on the oil aged silica surface (at 70 °C) are shown in Fig. 5. A longer aging time result in more oil wetness of the surface in comparison to a shorter aging time. It can be observed from Fig. 5 that exposure to low salinity water can shift the wettability of a silicate mineral surface towards water wet regime and this effect is highly prominent when further exposed to a low salinity surfactant solution. However, a lower divalent to monovalent ion ratio in the low salinity surfactant formulation can result in more water-wetness of the mineral surface for a sufficiently long-aged surface.

5 Oil Recovery Potential of Low Salinity Surfactant Formulations

The oil recovery efficiency of any novel EOR technique requires its laboratory-scale evaluation before it is tested in the field. The oil recovery efficiency is generally tested in laboratory though core flooding experiments using rock and fluid samples at pressure and temperature conditions representative of a reservoir. Unlike low salinity water flooding, the low salinity surfactant flooding has not been extensively evaluated through core flooding experiments. It has only been studied by a few researchers in the last decade. Also, pilot/field-scale testing has not been performed yet by any oil company. The detail on the limited number of core flooding studies

of low salinity water flooding performed by researchers is presented in Table 2. The reported results of core flooding suggested that application low salinity surfactant flooding can increase the oil recovery which is found to vary between 3 to 32% of OOIP over secondary water flooding. The low salinity surfactant flooding has been tested in two different modes: low salinity surfactant is tailored behind a low salinity water flooding in secondary mode and low salinity surfactant flooding after high salinity secondary water flooding. Although incremental oil volume was produced in both cases the former resulted in higher incremental oil recovery as seen from Table 2. Figure 6a presents the recovery profile showing both test mode.

Again the ratio of divalent to monovalent metal cations in both low salinity brine and low salinity surfactant solution observed to influence the incremental recovery by low salinity surfactant injection. An increase in the relative concentration of divalent

Table 2 Summary on low salinity surfactant core flooding studies conducted by different research groups using various formulations along with their obtained recovery efficiencies

Sl. No.	Low salinity surfactant formulation for tertiary flood	Secondary waterflood	Chase brine flood	Crude oil and core used	Incremental oil recovery (% OOIP)	Source
1	5000 ppm NaCl + ENORDET 0242L (an	5000 ppm NaCl	No chase brine flood	Crude with TAN = 2.84 and TBN = 0.95 Berea sandstone	30–32	[2]
2	Olefin sulfonate from Shell Chemicals) + 10,000 wt % isoamyl alcohol (IAA)	Synthetic water, TDS = 32321 ppm			20	
3	31,051 ppm NaCl + 500 ppm SDBS	3250 ppm NaCl	No chase brine flood	Crude with API gravity = 33 ⁰ TAN = 1.08 and TBN = 1.16 Berea sandstone	3	[25]
4	3087 ppm NaCl + 136 ppm CaCl ₂ + 500 ppm SDBS	3087 ppm NaCl + 136 ppm CaCl ₂			5.1	
5	2825 ppm NaCl + 221 ppm CaCl ₂ + 30 ppm MgCl ₂ + 500 ppm SDBS	2825 ppm NaCl + 221 ppm CaCl ₂ + 30 ppm MgCl ₂			5.4	
6	31,051 ppm NaCl + 5000 ppm S3 (an alkylbenzenesulfonate surfactant with chain length C ₁₅ to C ₁₈)	3087 ppm NaCl + 136 ppm CaCl ₂	32,500 ppm NaCl		27.1	[26]
7	3087 ppm NaCl + 136 ppm CaCl ₂ + 5000 ppm S3	3087 ppm NaCl + 136 ppm CaCl ₂	30,875 ppm NaCl + 1362 ppm CaCl ₂		27	

'OOIP' stands for original oil in place

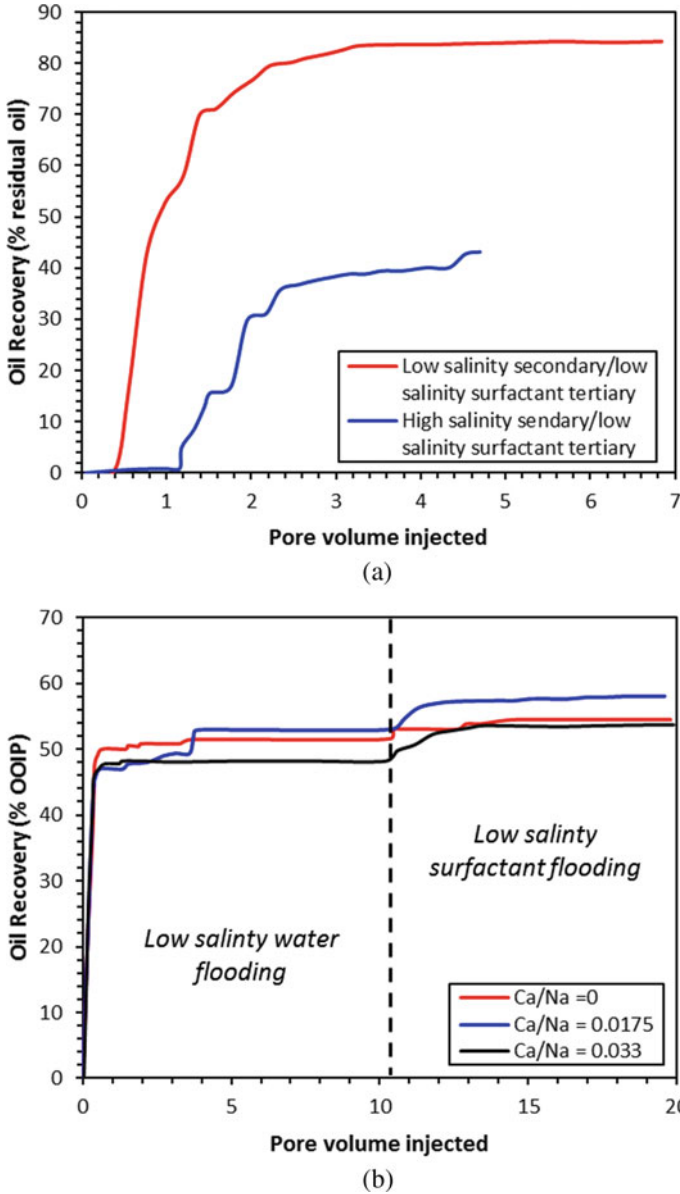


Fig. 6 Oil recovery profile as function of pore volume injected **a** comparison of low salinity surfactant flooding with low and high salinity secondary flood (Sl. No. 1 and 2 of Table 2) (“Adapted with permission from Alagic and Skauge [37]. Copyright 2010 American chemical society.”), **b** comparison of low salinity surfactant flooding for varying divalent to monovalent ratio of metal cation (Sl. No. 3–5 of Table 1). (“Adapted with permission from Khanamiri et al. [14]. Copyright 2016 American chemical society”)

metal cations in low salinity preflush, as well as low salinity surfactant formulation, resulted in slightly higher incremental recovery (Table 2). The oil recovery profile for different divalent to monovalent cation ratio is presented in Fig. 6b.

When high salinity water is injected as chase brine after low salinity surfactant injection it results in small incremental oil recovery. However, the influence of the composition of the chase brine in terms of divalent to monovalent cation on the oil recovery is negligible.

6 Mechanism of Low Salinity Surfactant EOR

As a hybrid EOR method, low salinity surfactant flooding works through a set of complex mechanisms which are a combination of both low salinity mechanism and surfactant flooding mechanism. The low salinity surfactant solution resulted in a lower oil–water interfacial tension in the oil reservoir in comparison to high salinity surfactant injection due to: (a) higher CMC resulting in delayed micellization; (b) bilayer formation at optimum salt concentration due to charge shielding of surfactant head groups resulting in a tight packing at the interface; (c) lower surfactant aggregation number resulting in lamellar aggregation of surfactant molecules at the interface. A lower interfacial tension between oil and low salinity surfactant solution increases the capillary number (an example shown in Table 3). However, the residual oil saturation after low salinity surfactant flooding (e.g., first case cited in Table 3 resulted in residual oil saturation 6 to 4% of OOIP) is much lower than residual oil saturation which could be achieved according to capillary number theory (40% for the above-mentioned case [53]).

An increase in reservoir pH is a predominant effect associated with low salinity water flooding as evident from various laboratory core flooding reports [6, 11, 15, 27]. Injection of low salinity water into a reservoir that originally contains high salinity formation water causes disturbance to a pre-existing chemical equilibrium established in the crude oil-rock-brine system. High salinity formation water results in the formation of organo-metallic complexes where divalent cation acts as a bridge to

Table 3 Capillary number (N_c) before and after low salinity surfactant injection

Low Salinity surfactant formulation	Secondary water flood composition	N_c during secondary low/ high water flood	N_c during low salinity surfactant flooding
5000 ppm NaCl + ENORDET 0242L (an Olefin sulfonate from Shell Chemicals) + 10,000 wt % isoamyl alcohol (IAA)	5000 ppm NaCl	9.5×10^{-8}	2.2×10^{-4}
	Synthetic water, TDS = 32321 ppm	7.5×10^{-8}	2.2×10^{-4}

(“Adapted with permission from Alagic and Skauge [37]. Copyright 2010 American chemical society”)

bind negatively charged crude oil molecules to the negatively charged silicate surface of sandstone rock. Low salinity water breaks this kind of complexes and results in the release of divalent cations from the rock or clay surface to re-established chemical equilibrium. The surrounding water molecules dissociate in this process into H^+ and OH^- ions. H^+ ions due to their higher affinity for clay and also to substitute divalent cations adsorbed onto the silicate or clay surface. Thus, OH^- ions remain in solution with increasing pH. With the injection of low salinity surfactant solution, the reservoir pH can further increase as evident from the effluent brine analysis performed by Alagic et al. [54] as shown in Fig. 7. An increase in the pH causes the following effects: (a) saponification of natural alkaline reactive compounds in crude oil, (b) Increasing surface activity of asphaltene. Crude oil consists of saponifiable alkaline reactive components known as petroleum acid. These petroleum acids are also known as nathenic acid which represents an unspecified mixture, of which carboxylic acids are the dominant constituents. Other, components include carboxyphenols, porphyrins, and asphaltene. A reaction between petroleum acids and their subsequent hydrolysis resulted in the generation of insoluble surfactant [55]. The generated surfactant can act in three different ways: reduce interfacial tension, alter reservoir rock wettability and cause emulsification. Again, at high or low pH the functional groups of asphaltene molecules become charged. It results in increased hydrophilic behavior and enhances their surface activity thereby reduces the interfacial tension. The effect of pH on the

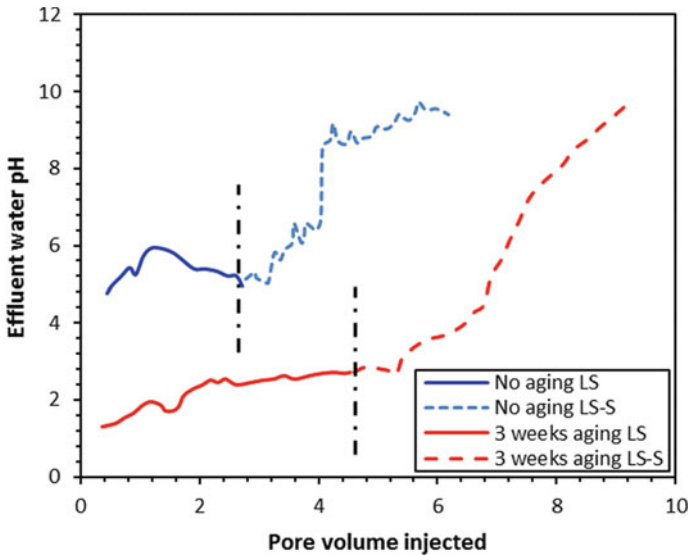


Fig. 7 Variation in effluent pH as function of pore volume injected during low salinity (LS) and subsequent low salinity surfactant (LS-S) flooding for cores (Berea sandstone) with and without aging case. Composition of low salinity water: 5000 ppm; low salinity surfactant solution: 5000 ppm NaCl + 10000 ppm Enordet O242L (an internal olefin sulfonate) +5000 ppm iso-amyl alcohol. (“Adapted with permission from Alagic et al. [54]. Copyright 2011 Elsevier”)

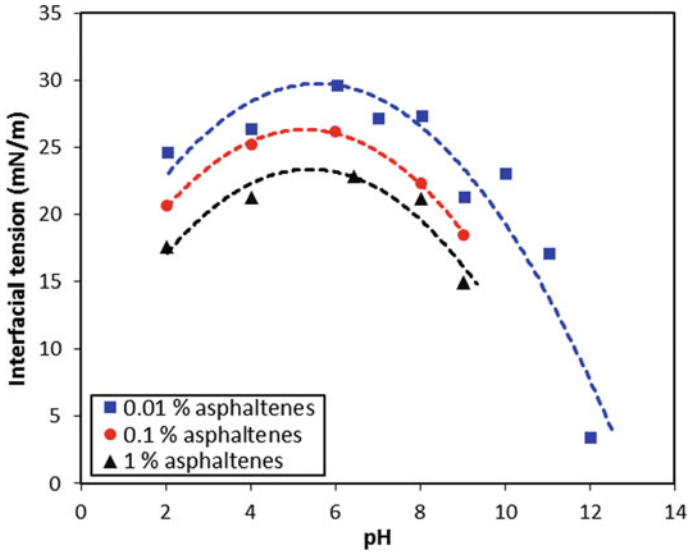


Fig. 8 Oil water between interfacial tension model oil (toluene + asphaltene in 0.01, 0.1, 1.0 wt %) and water as function of pH (“Adapted with permission from Poteau et al. [56]. Copyright 2005 American chemical society”)

interfacial tension between a model oil (containing asphaltene) and water is shown in Fig. 8. Though this effect also observed at low pH, it is more prominent at high pH because asphaltene molecules consist of more acidic functional groups as compared to basic functional groups [56]. A high and low pH cause reduce coalescence of water and oil droplets and stabilize oil–water emulsions formed by injected surfactant solution.

A high salinity condition promotes the formation of the water-in-oil emulsion and the surfactant moves over to the oleic phase. An increasing salinity gradient resulted in trapping of surfactant molecules in the oil phase and causes a delayed surfactant breakthrough. On the other hand, a low salinity environment in the reservoir causes surfactants to stay in the aqueous phase and form micro-emulsion by solubilizing oil in water, thus it increases the oil recovery efficiency of the surfactant solution.

Adsorption of surfactant on the rock-forming mineral surface causes an increase in hydrophobicity and thus causes higher oil wetness of a surface [57]. High salinity conditions are known to result in high surfactant adsorption irrespective of the concentration of surfactant. For example, anionic surfactants are widely used for sandstone reservoirs to reduce adsorption due to the similarities in their similar charges; but at high salinity condition the cations in water help in binding of negatively charged anionic surfactant molecules with negatively charged sandstone surface thus promotes its adsorption [58]. Also, high salinity causes precipitation of anionic surfactants and subsequent adsorption of it on the reservoir rock surface [59]. Low salinity surfactant combination thus lowers surfactant adsorption and causes

increased water wetness of the reservoir rock. Moreover, the surfactant adsorption also depends on the reservoir pH. An increasing pH causes a sandstone surface to become more negatively charged and thus reduces the adsorption of surfactant [60]. Since low salinity surfactant injection results in increased pH, it further lowers the adsorption of surfactant and promote water wetness. The increased water wetness directly due to low salinity water and as well as due to pH increase, enhances the oil recovery of the low salinity surfactant flooding process. In addition, the wettability is also influenced by the relative concentration of divalent ions in the low salinity surfactant formulation. The presence of divalent ions forms cross-linked aggregations which result in increased elastic modulus of the oil–water interface. Subsequently, a higher elastic modulus of the interface between crude oil and low salinity surfactant solution causes bypassing of the oil by surfactant solution as a result of the smaller strain of the interface [61].

7 Conclusion

Combining novel low salinity water flooding with conventional surfactant flooding can be an effective EOR solution. The synergism of low salinity water flooding and surfactant flooding can greatly impact the reservoir properties and thus improves the oil displacement process. Although a few studies have been published on low salinity surfactant flooding very interesting observations were made in these studies. Low salinity surfactant solutions were able to produce ultra-low oil–water interfacial tension without the application of a co-surfactant. The presence of divalent ions in the low salinity surfactant solution further suppress the interfacial tension values. The pH of the low salinity surfactant solution impacts the interfacial tension values depending on the ionic strength of the solution. Comparison between SDBS and AOT showed low salinity surfactant formulations containing AOT result in much lower interfacial tension as compared to SDBS. Low salinity surfactant solutions can also change the wettability of reservoir rock from oil-wet to water-wet regime. A lower relative concentration of divalent ions can result in a greater shift towards water-wet regime. Laboratory core flooding studies show that a significantly high incremental oil recovery (as high as 32% of OOIP) can be achieved with low salinity surfactant flooding. A complex interplay of physicochemical mechanisms involved in the oil recovery process through low salinity surfactant flooding including interfacial bilayer formation, lamellar surfactant aggregation, insitu soap generation, wetting alteration, oil in water solubilisation etc. However, further research is needed to understand the process and to optimize low salinity surfactant formulations to maximize oil recovery.

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