

Thermal Stability and Compatibility of Surfactants in Presence of Formation Water Salinity under Reservoir Conditions

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ABSTRACT

In the surfactant alternating gas injection, the injected surfactant slug is remained several days under reservoir temperature and salinity conditions. As reservoir temperature is always greater than surface temperature. Therefore, thermal stability of selected surfactants use in the oil industry is almost important for achieving their long-term efficiency. The study deals with the screening of individual and blended surfactants for the applications of enhanced oil recovery that control the gas mobility during the surfactant alternating gas injection. The objective is to check the surfactant compatibility in the presence of formation water under reservoir temperature of 90°C and 120°C. The effects of temperature and salinity on used surfactant solutions were investigated. Anionic surfactant Alpha Olefin Sulfonate (AOS_{C14-16}) and Internal Olefin Sulfonate (IOS_{C15-18}) were selected as primary surfactants. Thermal stability test of AOS_{C14-16} with different formation water salinity was tested at 90°C and 120°C. Experimental result shows that, no precipitation was observed by surfactant AOS_{C14-16} when tested with different salinity at 90°C and 120°C. Addition of amphoteric surfactant Lauramidopropylamide Oxide (LMDO) with AOS_{C14-16} improves the stability in the high percentage of salinity at same temperature, whereas, the surfactant blend of IOS_{C15-18} and Alcohol Aloxyl Sulphate (AAS) was resulted unstable. The solubility and chemical stability at high temperature and high salinity condition is improved by the blend of AOS_{C14-16}+LMDO surfactant solution. This blend of surfactant solution will help for generating stable foam for gas mobility control in the methods of chemical Enhanced Oil Recovery (EOR).

Keywords: Divalent Ions, Foam, Surfactant, Salinity, Surfactant Alternating Gas, Thermal Stability.

1. INTRODUCTION

After primary and secondary oil recovery methods, about one third of the Original Oil in Place (OOIP) are remained in the pore channels of existing reservoirs due to the decline in pressure. This remained oil can be displaced from the pore channels towards the producing well by the techniques of EOR [1-2]. Thermal Stability is critical at the surface and in the reservoir conditions because surfactants are sensitive at temperature and salinity. Each reservoir has its own temperature and salinity range therefore; selection of

foam forming surfactants must be stable in reservoir conditions [3]. Wettability is the most important factor in the secondary oil recovery process. Wettability alteration of reservoir rock with surfactant resulted improve the flow and fluid distribution in a pore channels of reservoir. The presence of brine water in the pore channels of the reservoir and its properties can influence the wettability and irreducible water saturation that affect the function of relative permeability. Formation water (brine water) is treated as a separate phase when used in the equations of reservoir fluid flow. The water alternating gas

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injection process suffers by gravity override and fingering problems in the heterogeneous oil produced reservoirs. The oil recovery remains low during the Water alternating gas injection process. The solution of improving oil recovery by this process is the addition of surfactants in brine water that reduces the problems of gravity override and fingering, therefore, improving the sweep efficiency (enhancing the oil production). Anionic surfactants are mostly used in the oil industry due to its low adsorption on rock, good foamability, biodegradability and stability in the presence of salinity and crude oil. Anionic surfactant Alpha Olefin Sulfonate is generally preferred due to its wetting characteristics (because of modification in the water-wet system) and good foaming properties in crude oil. Further, this type of surfactant provides extra ordinary detergency and biodegradability [4]. Non-ionic surfactants precipitate above the cloud point temperature because of its hydrogen bonding with water becomes weaker and their temperature reduces with salinity [5-7]. To overcome the problems of solubility and chemical stability anionic surfactants are used mostly at high temperature.

1.1 Temperature Effect

The most of surfactant solution have cloud point temperature (the temperature above which an aqueous solution of surfactant becomes cloud) beyond which the solution becomes cloudy. The cloudy surfactant solution due to the temperature limit is not used further for any parameter measurement. The anionic surfactants have Kraft point temperature (minimum temperature at which surfactants forms micelles). If the temperature is lower than the Kraft point temperature, surfactant solution becomes ineffective and drops out of the aqueous solution [8]. The cloud point temperature range 30 -160°C depending upon the structure of surfactant. However, the temperature plays a minor role for a blended surfactant system due to their synergism [9]. The temperature above 120°C results in either degradation or precipitation of surfactants. The precipitation of surfactant in the brine water is unfavorable in the application of EOR [10].

1.2 Salinity Effect

Surfactant cannot work better in the high salinity environment. Therefore, the selection of particular

surfactant should have an optimum salinity level at which oil and water can be equally solubilized into a micro emulsion [11]. Also the capacity of water solubilization for a particular micro emulsion is narrowly related to the partition of co-surfactants between water, oil and interfaces, chain length and nature of crude oil [11-13]. However, the design of appropriate surfactants at high temperatures (from 70-120°C) and high salinity condition is challenging due to limitations in solubility and chemical stability [14-15]. In this study, the individual and blended surfactant solution prepared in the different brine water salinity and tested at 90 and 120°C to prevent the surfactant precipitation.

2. MATERIALS

Anionic surfactant AOS_{C14-16}, IOS_{C15-18}, AAS and amphoteric surfactant LMDO are used in this study. Salts (sodium chloride, magnesium chloride and calcium chloride) are used for preparing synthetic brine water with different salinity. Tables 1-2 show the ionic composition of synthetic (laboratory prepared) brine water.

Table 1: Composition of Synthetic Brine Water for Surfactant AOS_{C14-16}

Salt (ppm)	Brine Water (A)	Brine Water (B)	Brine Water (C)
Sodium	27521.367	19658.119	11794.87
Chloride	49400.76	39532.17	30071.648
Calcium	2522.52	3603.60	4324.324
Magnesium	836.69	956.22	1434.33

3. METHODOLOGY

The first step of experiment is related to the testing of surfactant solutions for aqueous stability. The surfactant solution was mixed with maximum brine salinity at high temperature. 10ml of each concentrated solution of surfactant was taken in a glass test tube, and then allowed to settle for an hour in an oven at reservoir temperature of 90 and 120°C. The surfactant solution was considered stable when no phase separation or clouds has been observed. Fig. 1(a) shows the experimental setup of thermal stability of tested samples and Fig. 1(b) shows the clear surfactant solutions (no clouds and no precipitates shown in the test tubes).

Salt (ppm)	Brine Water (A)	Brine Water (B)	Brine Water (C)	Brine Water (D)	Brine Water (E)
Na	19658.119	27521.367	35384.615	47179.487	58974.358
Cl	45175.037	57311.789	64504.152	76717.185	91025.641
Ca	5405.405	5405.405	3603.603	1801.801	-
Mg	1792.916	1792.916	1195.277	239.408	-
Total brine salinity (ppm)	72031.477	92031.477	104687.647	125937.881	150000

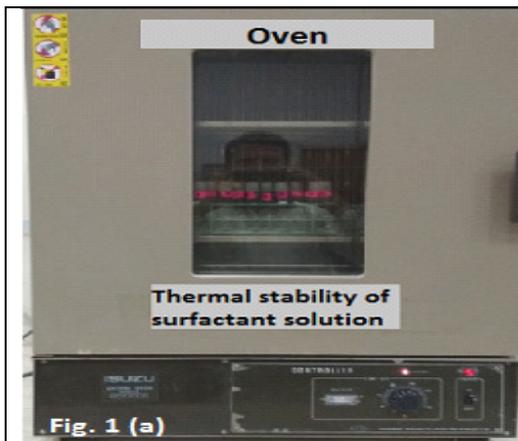


Fig. 1(a): Thermal/Aqueous Stability Experimental Setup

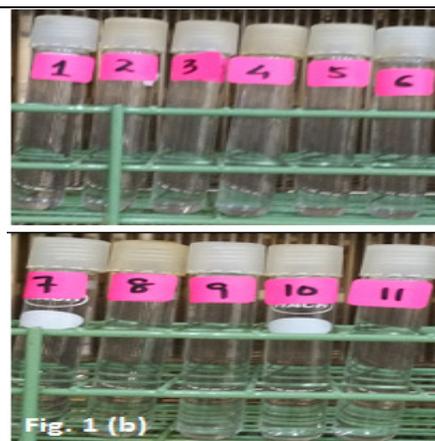


Fig. 1 (b): Clear Surfactant Solutions

4. RESULTS AND DISCUSSION

Low and high concentration of AOS_{C14-16} was tested in the presence of different brine salinities with divalent ions. The solution was tested with Brine-A, Brine-B and Brine-C as shown in the Table 1. From the aqueous thermal stability test, AOS_{C14-16} was stable in maximum brine salinity of 80281.4ppm (Brine-A) with minimum divalent ions at temperature 90 and 120°C for an hour. When the percentage of divalent ions were increased to 3603.60ppm of Ca⁺⁺, and 956.22ppm of Mg⁺⁺ ions (Brine-B), the AOS_{C14-16} solution remained stable and no cloud was observed at 90 and 120°C. Increasing the percentage of divalent ions with AOS_{C14-16} solution at low and high concentration led to a decrease in the percentage of monovalent ions (Na ions and Cl ions). In Brine-C, the percentage of divalent ions was increased as 4324.32ppm of Ca⁺⁺ ions and 1434.3ppm of Mg⁺⁺ ions resulted into decrease in monovalent ions. The AOS_{C14-16} was stable in the maximum divalent ions for the composition of (Brine-C) as compared to the composition of (Brine-A and Brine-B). Therefore, the stability test result shows that, the surfactant AOS_{C14-16} was soluble in the total brine salinity of 80281.4ppm

with 2522.52ppm of Ca⁺⁺ ions and 836.69ppm of Mg⁺⁺ ions at 90°C and 120°C. No precipitation and clouds were shown. Stability was generated due to the hydrogen bonds that formed between the head groups, i.e. when the polar head group has a hydrogen bond donor and proton acceptor [16-18].

Equal concentration of AOS_{C14-16} was blended with LMDO to maximize the range of divalent ions. As AOS_{C14-16} is limited to the salinity and LMDO is tolerant to divalent ions. The blend of surfactant solution was tested with Brine-A to Brine-E as shown in the Table 2. Low concentration of this surfactant blend solution was tested and resulted unstable in presence of high brine salinity at 90 and 120°C, but the same blend was tested in the low brine salinity (Brine-A) and shown stable at same conditions. High concentration of this blend was tested and observed stable in Brine-B-E at 90°C and 120°C. This surfactant blend solution showed long term thermal stability. No clouds were shown. Table 3 shows different concentration of AOS_{C14-16} and blend of AOS_{C14-16} with LMDO surfactant in the presence of brine salinity. Low and high concentration of IOS_{C15-18} was

blended with AAS. Additive AAS was used due to its excellent divalent ion tolerance. The result showed clouds in the both tested solution and this surfactant blend was considered unstable in the Brine-A-E. The instability in the both solution of this surfactant blend is due to the limited solubility in the brine water.

The percentage of brine salinity was increased due to the synergy of the AOS_{C14-16} and LMDO surfactant. Therefore, the blend of AOS_{C14-16} and LMDO surfactant solution was stable in the maximum brine salinity of 125937.881ppm with 1801.801ppm of Ca⁺⁺ ions and 239.408ppm of Mg⁺⁺ ions at 90°C and 120°C. Further, the same concentration of this blended surfactant was tested in presence of 150000ppm (Brine-E) without divalent ions. No precipitation and clouds were shown in the test tube. Formation brines with maximum divalent ions are generally considered as difficult targets. Surfactant blend solution exhibited good salt tolerance. Blend of AOS_{C14-16} and LMDO was shown good stability in presence of such reservoir conditions.

5. CONCLUSIONS

1. Individual surfactant AOS_{C14-16} was stable in maximum salinity of 80281ppm at 90 and 120°C. No clouds or precipitation was observed.
2. Blend of surfactant solution IOS_{C15-18}+AAS showed clouds in Brine Water-A-E.
3. Surfactant blend with low and high concentration of AOS_{C14-16}+LMDO showed good tolerance in salt concentration and thermal stability in the aqueous phase. Interfacial tension and core flood tests are recommended to validate the performance of surfactants.

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Table 3: Thermal Stability of Blended Surfactants at 90°C & 120°C in the Brine Water of Table 2

Surfactant Concentration (wt%)	Brine Water (A)	Brine Water (B)	Brine Water (C)	Brine Water (D)	Brine Water (E)
0.2%AOS _{C14-16} +0.2% LMDO	Stable	Not Stable	Not Stable	Not Stable	Not Stable
0.6%AOS _{C14-16} +0.6% LMDO		Stable	Stable	Stable	Stable
0.2%IOS _{C15-18} +0.2% AAS	Not Stable				
0.6%IOS _{C15-18} +0.6% AAS					

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