



# Journal of Applied Sciences

ISSN 1812-5654

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## Solubility of Foam Surfactants in High Divalent Ions at High Temperature

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**Abstract:** In Water Alternating Gas (WAG) injection processes, injected gas suffers from poor sweep efficiency due to low gas density, low gas viscosity leading to gravity segregation, override and viscous fingering. The oil recovery during the process remains low due to the problems of gravity segregation and viscous fingering. Foam surfactant is used to reduce gas mobility by increasing its apparent viscosity and improve volumetric sweep efficiency but the foam efficiency decreases in the presence of crude oil, divalent ions and high reservoir temperature. The main objective of this study is the screening of foam forming surfactants for CO<sub>2</sub> mobility control during water alternating gas injection process in the presence of maximum divalent ions at high temperature. Alpha Olefin Sulfonate (AOS) was selected as main surfactant. Solubility test of AOS with different brine was performed at 120°C. AOS was stable in the total brine salinity of 78568 ppm with 3265 ppm of calcium ions and 1434 ppm of magnesium ions. To maximize the range of divalent ions, Lauramidopropylamide Oxide (LMDO) was blended with AOS. The solution was stable in the presence of total salinity 78358 ppm with 4082 ppm of calcium ions and 1793 ppm of magnesium ions at 120°C. The aqueous stability over a range of divalent ions and temperature was improved by blend of surfactants and this will help for generating stable foam for CO<sub>2</sub> mobility control.

**Key words:** Surfactant, divalent ions, solubility, water alternate gas, foam

### INTRODUCTION

Some of the global oil reservoirs are producing at high temperature and high brine salinity with high percentage of divalent ions. The high temperature and high divalent ions pose major challenges for proper selection of foam surfactants. Foam in the reservoirs was first proposed by Bond and Holbrook and reported by Bernard and Holm in 1964. Foam can be defined as “A scattered system with bubbles that are separated by foam film and plateau boarders”. The foam begins to breakdown in its formation due to different circumstances, such as; film thinning, liquid drainage due to gravity, gas diffusion from smaller to large bubbles, interacts with the walls of its container, rupturing and coalescence (Karakashev and Grozdanova, 2012). Foam can be used:

- For plugging of unwanted phases and the near wellbore flow treatments such as foam-acid matrix stimulation in the reservoir
- In fracturing fluids
- In the shallow subsurface environmental improvement
- In EOR processes, foam can be used to overcome *in situ* permeability variations and gas mobility control

This method of foam can be applied by alternating gas with surfactant solution or by simultaneously injected gas and surfactant solution (Dholkawala *et al.*, 2007).

Much oil is left after water flooding because of the dominance of capillary forces over viscous forces. The trapped oil can be recovered by increasing the viscosity of displacing fluid and lowering the IFT between crude oil and drive water. Surfactants have been used for tertiary oil recovery for more than 35 years mostly in USA in depleted oil reservoirs after water flooding (Lv *et al.*, 2011). Foam surfactant mobilizes the trapped oil left after water flooding. The foam forming surfactants must be efficient and able to produce good quality and stable foam in contact with crude oil, brine salinity with divalent ions at particular reservoir temperature and controlling the gas mobility (Zhu *et al.*, 1998).

In the chemical EOR, anionic surfactants are widely used because of their low adsorption on sandstone reservoirs. AOS (C<sub>12-14</sub>) and AOS (C<sub>14-16</sub>) anionic surfactants are proved to be an excellent foam insensitive to brine composition and tolerant to presence of crude oil (Cubillos *et al.*, 2012). Nonionic surfactants are used as co-surfactants to improve system phase behavior. These types of surfactant are more tolerant to high salinity but cannot reduce much IFT as anionic surfactants. Amphoteric surfactants also known as zwitterionic

surfactants are temperature and salinity tolerant. Amphoteric surfactant was used for medium to high viscosity crude oil, Lauryl betaine was blended with 4:1 blend of Neodol67-7PO sulfate and IOSe<sub>15-18</sub>. This was tested in the secondary and tertiary oil recovery with effective mobility control and oil displacement (Farajzadeh *et al.*, 2012).

In 1956-1957, the first field pilot of Water Alternating Gas (WAG) was implemented in the North Pembina field, Alberta, Canada (Algharib *et al.*, 2007; Nadeson *et al.*, 2004). Controlling the gas fingering in water alternating gas injection process foam surfactants is more efficient than water. Aqueous permeability can be decreased by increasing gas saturation. In addition to produce foam with low potential cost effective process, the low concentrations of surfactant are required. In the low permeable formation gas breakthrough introduces, that does not receive more surfactant to support the foam deep into the formation (Liu *et al.*, 2011). In addition to meet the reservoir condition, selected foam surfactant must be able to develop ultralow IFT with crude oil, have low adsorption and form clear single phase aqueous solution.

AOS was good foam forming surfactant and was implemented in many oil reservoirs (Puerto *et al.*, 2012). In the North Sea, Alpha Olefin Sulfonates (AOS) have been successfully used as foaming agents for controlling gas mobility. The foam assisted WAG was implemented in the sandstone reservoirs at the Snore field, North Sea (Skauge *et al.*, 2002; Blaker *et al.*, 2002; Aarra *et al.*, 2002). In a foam assisted water alternate gas injection process, foam surfactant is added to the aqueous solution that is injected alternately with gas (Stevenson, 2012). During this injection process, the foam can improve the gas mobility control by three different ways:

- Minimizing the gravity segregation
- Minimizing early breakthrough
- Blocking the gas flow into completely swept zones

To determine the aqueous solubility and stability at temperature 120°C, blend of AOS and LMDO were used and tested in the presence of different percentage of divalent ions. LMDO can improve surfactant tolerance to high salinity with divalent ions. This study deals with blend of AOS and LMDO foam surfactant in the presence of high salinity with divalent ions at high temperature. No solubility problem was observed during the laboratory test.

### WAG PROJECTS IN MALAYSIA

More than billion of barrels of additional oil can be recovered through EOR methods (Samsudin *et al.*, 2005).

The chemical EOR was identified as one of the good potential for field implementation to increase oil recovery in Malaysia offshore fields. This is the screening and comprehensive EOR study conducted by PETRONAS on seventy two reservoirs (Samsudin *et al.*, 2005; Othman *et al.*, 2007). About 37% of OOIP is recovered through the entire life of mature reservoirs from the Malaysian offshore oil fields. These fields have been developed under conventional methods. Remaining oil about 63% from these mature reservoirs would not be recovered through the current production facilities. This is the main reason that Malaysia has motivated to implement EOR methods.

According to the performed experimental and simulation studies, immiscible WAG with high injection of CO<sub>2</sub> gas can improve an additional oil recovery factor. Compositional simulation model were prepared to analyze different injection strategies at immiscible conditions and infill locations to maximize oil recovery in Dulang field offshore Malaysia. A first successful WAG pilot was implemented in a sub block, South 3 Dulang field offshore Malaysia in 2002 (Drid and Tiab, 2004; Panda *et al.*, 2011). From the initial EOR, screening data water alternating gas is the most favorable EOR process for the offshore fields of Malaysia (Rosman *et al.*, 2011). In the light of initial EOR screening data for Baram Delta Operation, two WAG projects were selected. One WAG pilot project will start at the end of this year at Tapis and another one will start in 2016 at Guntong field offshore Malaysia (Abdullah *et al.*, 2011).

### MATERIALS AND METHODS

**Surfactants:** Alpha Olefin Sulfonate AOS<sub>C14-16</sub> and Lauramidopropylamide Oxide (LMDO) were gifted by Stepan Company USA.

**Salts for brine solution:** Sodium chloride (NaCl) was purchased from Fischer Company U.K, Magnesium chloride (MgCl<sub>2</sub>.6H<sub>2</sub>O) and Calcium chloride (CaCl<sub>2</sub>.2H<sub>2</sub>O) were purchased from R and M Chemicals U.K. Table 1 presents the composition of brine solution.

**Aqueous solubility test:** The first step of experiment is related to the testing of foam surfactant solution for aqueous solubility with maximum brine salinity with divalent ions at high temperature. Concentrated solution of surfactant and brine were mixed in a glass tube, agitated and then was allowed to settle for an hour in an oven at reservoir temperature of 120°C. This foam forming surfactant solution was considered stable when no phase separation or cloudiness has been observed.

Low and high concentration of AOS was tested in the presence of different brine salinities with divalent ions.

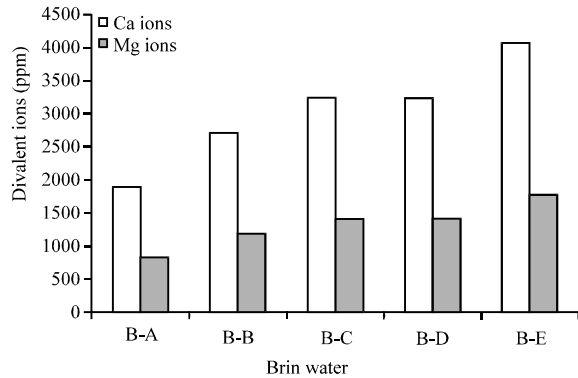


Fig. 1: Brine water with increase in divalent ions

Table 1: Composition of synthetic brine water

Salt (ppm)	Brine water				
	A	B	C	D	E
Sodium	27521	19658	11795	23590	23590
Chloride	48305	38664	28192	46397	48893
Calcium	1905	2721	3265	3265	4082
Magnesium	837	1195	1434	1434	1793
Total salinity	78568	62238	44686	74686	7835

Table 2: Solubility of AOS in divalent ions at high temperature

Surfactant concentration Wt (%)	Calcium ions (ppm)	Magnesium ions (ppm)	Solubility at 120°C
0.2AOS	1905	837	Clear
0.6AOS			
0.2AOS	2721	1195	Clear
0.6AOS			
0.2AOS	3265	1434	Clear
0.6AOS			
0.2AOS,0.2LMDO	3265	1434	Clear
0.6AOS,0.6LMDO			
0.2AOS,0.2LMDO	4082	1793	Clear
0.6AOS,0.6LMDO			

The solution was tested with Brine A, Brine B and Brine C as presented in Table 1. AOS was soluble in the total brine salinity of 78568 ppm with 3265 ppm of Ca<sup>++</sup> ions and 1434 ppm of Mg<sup>++</sup> ions at 120°C as presented in Fig. 1. No precipitation and clouds were shown.

Equal concentration of AOS was blended with LMDO to maximize the range of divalent ions. As AOS is limited to the salinity and LMDO, it is tolerant to divalent ions and foam stabilizer. The solution was tested with Brine D and Brine E at 120°C for 1 h. This blend was soluble and stable in the total brine salinity of 78358 ppm with 4082 ppm of Ca<sup>++</sup> ions and 1793 ppm of Mg<sup>++</sup> ions at 120°C. The presence of divalent ions was presented in Fig. 1. No precipitation and clouds were shown. Also at high concentration, of same surfactants was blended and tested. No clouds or precipitation was shown (Table 2).

## RESULTS AND DISCUSSION

From the aqueous solubility test, AOS was stable in maximum brine salinity of 78568 ppm (Brine A) with

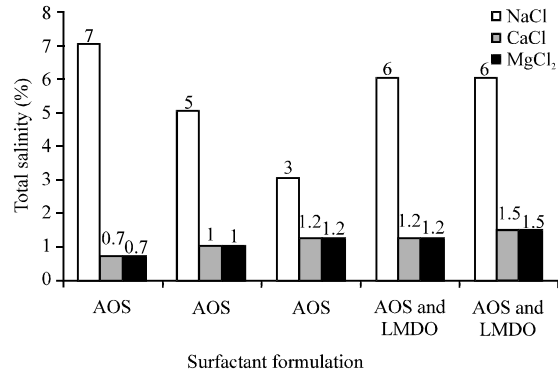


Fig. 2: Solubility of surfactant in different salinity with divalent ions at 120°C

minimum divalent ions at temperature 120°C for 1 h. When the percentage of divalent ions were increased to 2721 ppm of Ca<sup>++</sup> and 1195 ppm of Mg<sup>++</sup> ions (Brine B), the AOS solution remained stable and no cloud was observed at 120°C. Increasing the percentage of divalent ions with AOS solution at low and high concentration, led to a decrease in the percentage of monovalent ions. In brine C, the percentage of increased divalent ions as 3265 ppm of Ca<sup>++</sup> ions and 1434.3 ppm of Mg<sup>++</sup> ions resulted into decrease in monovalent ions. The AOS was stable in the maximum divalent ions for the composition of Brine C as compared to the composition of Brine A and Brine B.

Foams are considered unstable if the surfactant is not soluble in brine salinity. Increasing the percentage of divalent ions, AOS was blended with LMDO. When the total brine salinity was increased to 78358 ppm, low and high concentration of blend remained stable at 4082 ppm of Ca<sup>++</sup> and 1793 ppm of Mg<sup>++</sup> ions. The monovalent ion percentage was increased as 48893 ppm of chloride and 23590 ppm of Sodium ions (Brine D). The percentage of ions was increased due to the synergy of the surfactants. The solution was stable at 120°C. The same concentration of blend was tested in presence of same divalent ions as in the composition of Brine C but with increased percentage of monovalent ions as 46397 ppm of Chloride ions and 23590 ppm of Sodium ions (Brine D). The solution was stable and no clouds were observed at 120°C. The stability of AOS was increased with blend of equal concentration of LMDO. No solubility problem was observed in these tests even when equal salt concentration 1.5% of CaCl<sub>2</sub> and 1.5% of MgCl<sub>2</sub> with 6% of NaCl were tested at 120°C. The salt concentrations with divalent ions in different formulations are presented in Fig. 2. Formation brines with maximum divalent ions are considered as difficult targets. Blend of AOS and LMDO was shown good solubility in presence of such reservoir conditions.

## CONCLUSION

Aqueous solubility test of AOS was performed in total brine salinity of 78568 ppm at 120°C. The increased percentage of divalent ions in different brine water was shown clear and stable. To maximize the range of salinity, LMDO was blended with AOS. The solution was stable in the presence of total brine salinity of 78358 ppm with 4082 ppm of Ca<sup>++</sup> and 1793 ppm of Mg<sup>++</sup> ions at 120°C.

To overcome the problem of CO<sub>2</sub> mobility control during water alternating gas injection process, the research is in progress to generate the maximum foam and its stability in the presence of crude oil with maximum divalent ions.

## ACKNOWLEDGMENTS

We would like to acknowledge the Universiti Teknologi PETRONAS for supporting this study. The authors would like to thank Stepan Company USA who has provided the surfactant samples for research study.

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