

## Impact of Nano-Particles on Static Performance of Surfactant Foams

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**Abstract:** Nowadays stable foams frequently used in earth sciences and mainly in hydrology and petroleum engineering. Surfactant foam injection is a sophisticated way of enhanced oil recovery through wettability, viscosity and miscibility modification of reservoir rock and fluids. Foam modification and best foam selection based on static screening criteria of foam features; foamability (FA) and foam stability (FS) is of vital importance in foam injection design. Nano-particles (here alcohol-based nano-silica (NS) and water-based nano-zinc oxide (N-ZnO)) can improve surfactant foam features and it is necessary to investigate their effects on anionic, cationic and nonionic surfactant foams; here SDS, CTAB and LAE-7 respectively. Some contradictions between FA and FS results make it important to define a new definition considering FA and FS simultaneously here called static foam performance (SFP). Additionally, a correlation has been developed for checking of previous works results based on SFP concept. Results show that anionic surfactant; SDS foam has minimum FA, FS and SFP among all tested surfactants in presence of nano-particles and it is not a satisfying choice for foam processes. Addition of N-ZnO almost always increases the FA of surfactants. NS has negative effects on CTAB and SDS FAs for all concentrations, but intermediate concentrations of NS clearly show positive impact on nonionic surfactant; LAE-7.

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### 1. Introduction

Micro and nano technologies have already contributed significantly to technological advances in a number of industries, including the electronics, biomedical, pharmaceutical, materials and manufacturing, aerospace, photography, and more recently the energy industries. Micro and nano technologies have the potential to introduce revolutionary changes in several areas of the oil and gas industry, such as exploration, drilling, production, enhanced oil recovery, refining and distribution. For example, nanosensors might provide more detailed and accurate information about reservoirs; specially fabricated nanoparticles can be used for scale inhibition; structural nanomaterials could enable the development of petroleum industry equipment that is much lighter and more reliable and long-lasting; and nanomembranes could enhance the gas separation and removal of impurities from oil and gas streams. Other emerging applications of micro and nano technologies in the petroleum industry are new types of "smart fluids" for enhanced oil recovery (EOR) and drilling (Kong and Ohadi, 2010). Nano fluids can be designed by adding nano-sized particles in low volumetric fractions to a fluid. The nano particles modify the fluid properties, and suspensions of nano-sized particles can provide numerous advantages. Nano-sized particles can impart

sedimentary, thermal, optical, mechanical, electrical, rheological, and/or magnetic properties to a base material that can enhance its performance (Singh and Ahmed, 2010). An innovative drag reduction method was put forwarded to decrease the drag of laminar flows of water through rock's micro-channels and then decrease the injection pressure of flooding significantly. The solution containing hydrophobic nanoparticles of SiO<sub>2</sub> is injected into the micro-channels of reservoir (Di et al., 2010). Nanoparticles have been speculated as good in-situ agents for solving reservoir engineering problems. Some selected types of nanoparticles that are likely to be used include oxides of Aluminum, Zinc, Magnesium, Iron, Zirconium, Nickel, Tin and Silicon. It is therefore imperative to find out the effect of these nanoparticle oxides on oil recovery since this is the primary objective of the oil industry. These nanoparticles were used to conduct EOR experiments under surface conditions. Distilled water, brine, ethanol and diesel were used as the dispersing media for the nanoparticles (Ogolo et al., 2012). Nanoparticle-stabilized emulsions have attracted many researchers' attention in recent years due to many of their specific characteristics and advantages over conventional emulsions stabilized by surfactants or by colloidal particles. For example, the solid nanoparticles can be irreversibly attached to the oil-

water interface and form a rigid nanoparticle monolayer on the droplet surfaces, which induce highly stable emulsions. Those emulsions can withstand harsh conditions. Compared to colloidal particles, nanoparticles are one hundred times smaller, and emulsions stabilized by them can travel a long distance (Zhang et al., 2010).

Surface active agents (surfactants) are amphiphilic materials with a characteristic chemical structure consists of one or more hydrophilic and one or more hydrophobic groups in a single molecule. In the standard surfactant terminology, the hydrophilic portion or polar portion is called "head" group and the hydrophobic group called "tail". Surfactants change the surface properties/interface properties between two immiscible fluids, lowering the interfacial surface energy (Chen, 2011).

Based on the charge on the head group, surfactants are broadly divided into 4 categories: anionic (negatively charged head group), cationic (positively charged), amphoteric or zwitterionic (both positive and negative charge) and nonionic, as shown in Table 1. It is well known that cationic and anionic surfactants have the ability to interact and create so-called ion-pairs. Such surfactants have recently been studied in more detail and they are referred to as catanionic surfactant mixtures in the chemical literature (Eksborg and Lagerstrom, 1973).

Foam in porous media is a dispersed gaseous phase within a continuous aqueous phase comprised mainly of thin films known as lamellae. The lamellae are stabilized by adsorption of surfactant at the gas/liquid interfaces. Because foam has an effective viscosity much higher than that of gas, it has been investigated as a method for improving sweep efficiency in processes where gases such as steam or supercritical CO<sub>2</sub> are injected to improve oil recovery from underground formations. Foam can reduce viscous fingering and gravity override caused by the low viscosity and density of the gas. Moreover, since fluids flow preferentially into layers of high permeability in a heterogeneous formation, foam is preferentially formed there and greatly increases local resistance to flow, thereby diverting injected fluids to zones of lower permeability and improving process efficiency (Yan et al., 2006).

Numerous factors, such as the velocity of flow of the gas and liquid, the structure and the size of pores, etc. could influence transport of foam in porous medium. Among those factors, the dynamic stability of the foam film is an important and essential one, and there is a consanguineous connection between the dynamic stability of the foam film and the behavior of the surfactant in the surfactant layer.

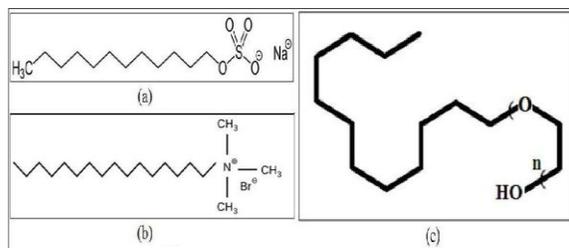
**Table 1.** Classification of Surfactants.

Class	Schematic	Example
Anionic		SDS
Cationic		CTAB
Amphoteric		CHAPS
Nonionic		LAE-7

Marangoni effect is well known to describe the dynamic elasticity of bilayer foam film and the same mechanism should exist at the dynamic process of foam flow in porous medium, in which the deformation of gas/liquid interface film happens frequently and constantly. And the dynamic elasticity of surfactant interface layer would also play a great role on the transport of foam out of question (Li et al., 2006). Solid particles can be used as emulsifying agents. Recent studies on solid particle-stabilized emulsions and foams show that very stable emulsions and foams can be formed by adsorption of nanoparticles at fluid-fluid interface with favourable contact angles. As a result, nanoparticle stabilized foams can be potentially more stable than foams stabilized by surfactants because particles can be essentially irreversibly adsorbed at a fluid-fluid, whereas surfactant molecules dynamically enter and leave the interface (Worthen et al., 2012). Vital factors of surfactant/gas/liquid systems are; foamability (generated foam volume for given fluid amount) and foam stability (remaining time of the generated foam or in other words; liquid drainage time).

## 2. Material and Methods

All the materials that have been used in this work, shown in Table 2, 3. Foams are produced of three different surfactant classes; anionic, cationic and nonionic. Additive nano-particles are nano-silica and nano-zinc oxide that are water dispersed and alcohol-based respectively.



**Figure 1.** Schematic of (a): SDS, (b): CTAB, (c): LAE-7 Structures.

**Table 2.** Characterization of Using Nano-Materials.

Using Name	Chemical Formula	Particle Size	Media
N-ZnO	ZnO	30-40 nm	Water Dispersed
NS	SiO <sub>2</sub>	30-40 nm	Alcohol-Based

**Table 3.** Characterization of Using Surfactants.

Surfactant	Abbreviation	CMC	Class
Sodium Dodecyl Sulfate	SDS	2400 PPM	Anionic
Cetyl Trimethyl Ammonium Bromide	CTAB	328 PPM	Cationic
Lauryl Alcohol Ethoxylate-7	LAE-7	700 PPM	Nonionic

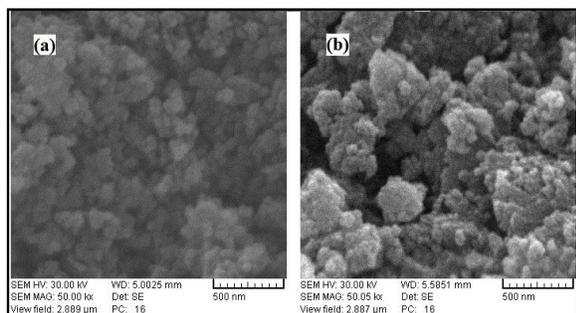


Figure 2. (a): SEM image of NS, (b): SEM image of N-ZnO.

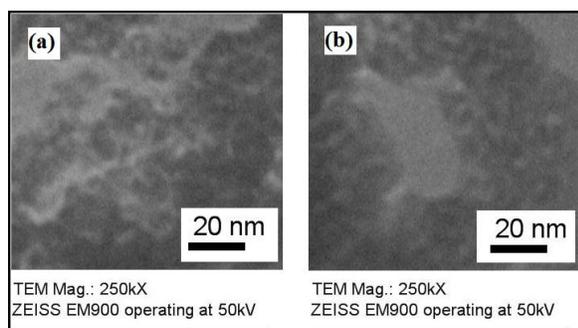
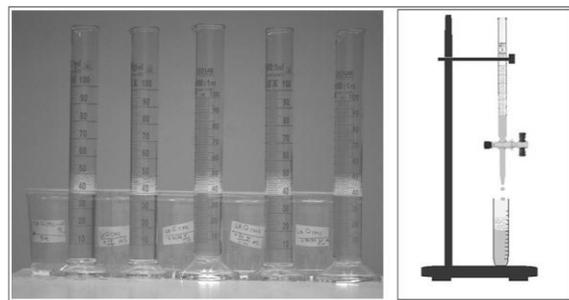


Figure 3. (a): TEM image of NS, (b): TEM image of N-ZnO.

### 3. Results

Nano-particle complimented surfactant fluids pour into a graduated cylinder in order to preparing foam and measuring foam volume and stability (at constant condition for all fluid samples). Each fluid sample is comprised of a surfactant and a nano-

particle with one of the following concentrations; 0, 0.1, 0.2, 0.4, 0.8 and 1.6 gram/100cc of NS and 0, 0.00125, 0.0025, 0.005 and 0.01 gram/100cc of N-ZnO.

**Figure 4.** Static Foam Test Facilities.

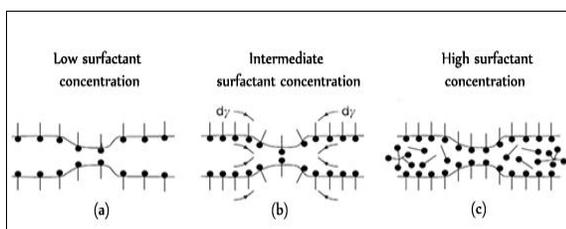
Based on Marangoni theory foam stability increases with increasing surfactant concentration up to a certain limit (often close to Critical Micelle Concentration (CMC), where foams are kinetically stable) above this limit; stability is not improved even if we increase surfactant concentration.

The Gibbs–Marangoni effect explains the maximum foaming behavior at intermediate surfactant concentration. This was illustrated in Figure 5. At low surfactant concentrations (well below the CMC) differential surface tension is relatively small and a disturbing forces cause poor foam. At very high surfactant concentration (well above the CMC), the differential tension relaxes too rapidly because of the supply of surfactant that diffuses to the surface (Figure 5 (c)). This causes the restoring force to have time to counteract the disturbing forces that produce a dangerously thinner film, and foaming is poor. Only at intermediate surfactant concentration range, maximum foaming is produced (Tadros, 2005).

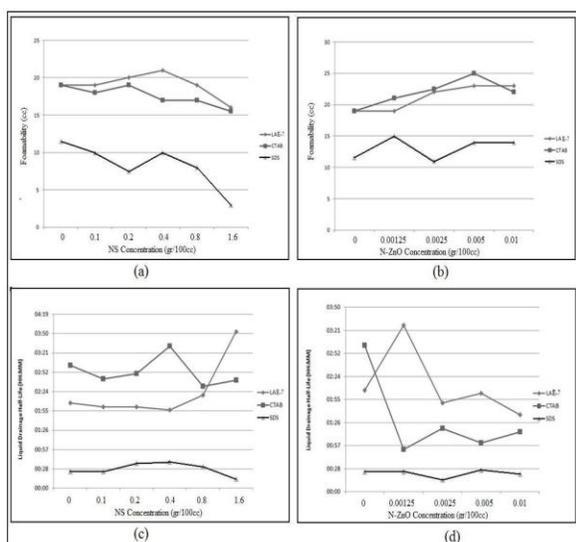
All foam tests conducted at surfactants CMCs (Table 3) having almost greatest foamabilities and foam stabilities. It was considered that liquid drainage half-life (taking time from  $V_{fi}$  "Initial Foam Volume" to  $V_{fi}/2$ ) to be a satisfying factor for foam stability. The initial volume of all surfactant foam samples selected equal to have a right comparison between them.

**Foamability:** Referring to equal diameters of graduated cylinders for all the tests, initial foam volume in cylinder was considered as foamability. As shown in Figure 6, NS and N-ZnO clearly affect the foamability for all three types of surfactants. SDS foam has the minimum foamability among all the surfactants. Despite LAE-7 foam, NS has a negative effect on CTAB and SDS foamabilities for all concentrations. Intermediate concentrations of NS clearly show positive impact on nonionic surfactant;

LAE-7. Despite NS effects, N-ZnO increases foamability for all surfactants (except for SDS at intermediate N-ZnO concentrations). Although SDS has the minimum foamability among all surfactant types, but its foamability difference to other surfactants is less than NS addition case.



**Figure 5.** Effect of Surfactant Concentration on Foam Stability; (a) Low Surfactant Concentration, (b) Intermediate Surfactant Concentration, (c) High Surfactant Concentration.



**Figure 6.** Effect of Various NS and N-ZnO Concentrations on Different Surfactants FAs and FSs.

**Foam Stability:** In all experimental foam studies, foam stability is of vital importance. Although some of surfactants have desirable foamabilities, but their limited stability, restricting their using broadness. Although, high concentrations of NS reduce the foamability of LAE-7, but that concentrations of NS can improve the foam stability. CTAB foam has a high stability at intermediate concentrations of NS. SDS foam has a lower stability than other surfactants (same as its foamability). CTAB foam has a higher stability than LAE-7 except for high NS concentrations. Considering higher foamability of LAE-7 than CTAB foam in presence of NS, we have a problem with selecting the best foam (higher foamability and lower stability). N-ZnO

decreases the CTAB foam stability considerably, especially in lowest tested concentration. As an amazing result, it was observed that; LAE-7 foam stability increases significantly in lowest N-ZnO concentration, but decreases in higher concentrations of N-ZnO. SDS foam stability is very low even in presence of N-ZnO particles. In N-ZnO complemented surfactants, LAE-7 foam has a higher stability than CTAB foam.

**Static Foam Performance:** Some mixtures have high foamabilities but low foam stabilities and sometimes the vice versa. In this dilemma we must define a new factor that considers both stability and foamability. In order to have a better foam selection, "Static Foam Performance (SFP)" has been defined here as; foam volume ( $V_f$ ) along the time (from foam generation time until liquid drainage half-life (LDH)).

$$SFP = \int_0^{LDH} V_f dt \approx \sum_{i=1}^n A_i \dots \dots \dots \text{(Equation 1)}$$

In which;  $i = 1, 2, \dots$  are integrated intervals and  $A_i$  is the area under the  $V_f$  vs. time curve in each interval.

Using this definition, foamability and foam stability are considered simultaneously.

Clearly NS improves the SFP of LAE-7, as shown in Figure 8; lowest and highest SFPs of LAE-7 are almost belonging to lowest and highest NS concentrations. In CTAB the curve trend shows that, intermediate concentrations of NS improve the SFP although larger concentrations lose its SFP obviously. In SDS foam, SFP curve trend is approximately same as the trend of CTAB curve, but in a smaller scale. SFP of NS complemented CTAB foam is almost always larger than LAE-7 (except for largest tested concentrations) and SDS intelligibly has a lower SFP than other surfactants.

In spite of NS effect, N-ZnO decreases the SFP of LAE-7, as shown in Figure 9, lowest and highest SFPs of LAE-7 are almost belong to highest and lowest N-ZnO concentrations. It means we must use N-ZnO gently in order to generate high performance foams. N-ZnO decreases CTAB SFP for all concentrations but its effect is larger for low concentrations. As an amazing result SDS shows a same SFP trend to LAE-7 again in a smaller scale.

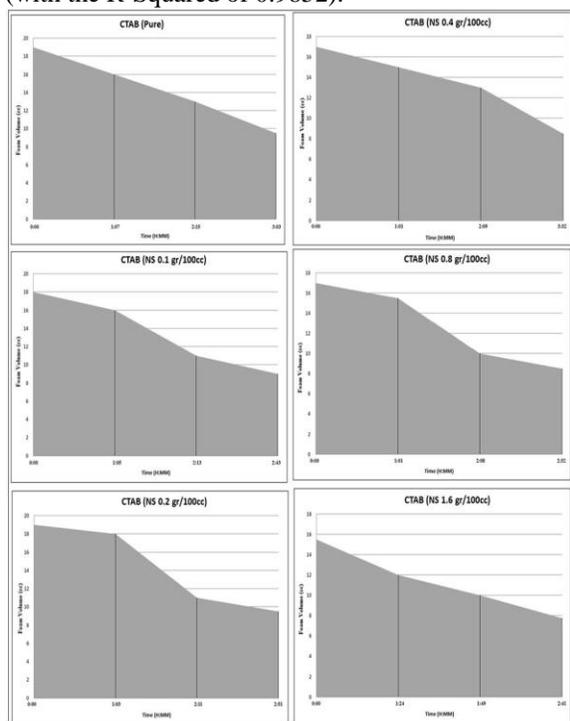
As an overall result, these experiments ensure that LAE-7 at low N-ZnO concentrations, CTAB at intermediate NS concentrations and LEA-7 at high NS concentrations have desirable SFPs and the best selected foam in this method is not same as foamability and foam stability methods results.

**Estimation of Static Foam Performance:** One main challenge with this new concept (SFP) is its lack of applicability for the previous researches, because to obtain this new factor it's needed to detect

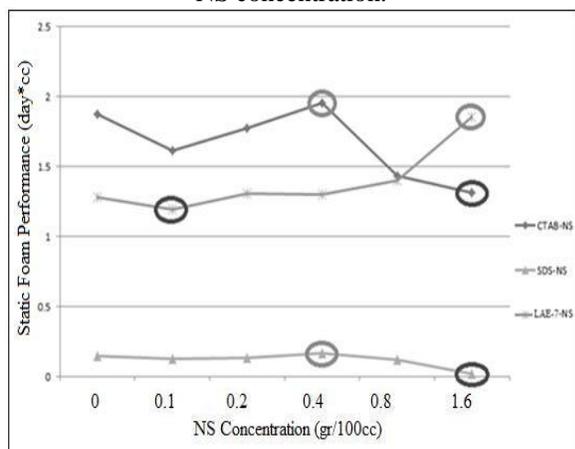
foam volume along the time until reach the LDH. To have the mentioned estimation of interest, a power form correlation is developed among SFP, foamability (FA) and foam stability (FS), useful at least for sensitivity analysis (because all the systems of foam generation are not the same; for example their foam containers are not in same diameters and/or foam generation methods are different). Generated correlation is as follows;

$$SFP = a \cdot FA^b \cdot FS^c \dots\dots\dots (Equation 2)$$

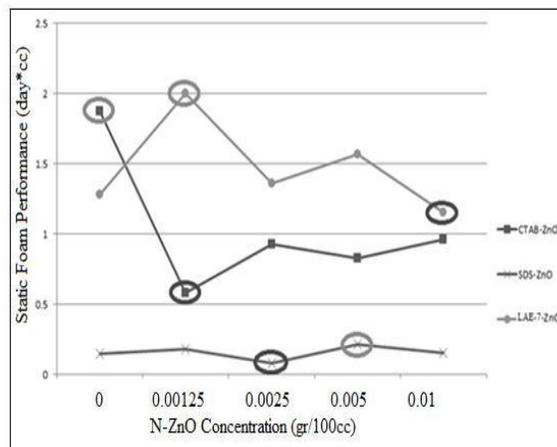
In which a, b and c are 0.6252, 0.9717 and 1.0486 respectively for the laboratory obtained data (with the R-Squared of 0.9852).



**Figure 7.** CTAB, Foam Volume vs. Time for Various NS concentration.



**Figure 8.** Effect of NS on Different Surfactants Static-Foam-Performance.



**Figure 9.** Effect of N-ZnO on Different Surfactants Static-Foam-Performance.

**4. Discussions**

Anionic surfactant; SDS foam has the minimum foamability, foam stability and SFP among all tested surfactants and it is not a satisfying choice for foam flooding processes.

NS has negative effects on CTAB and SDS foamabilities for all concentrations, but intermediate concentrations of NS clearly show positive impact on nonionic surfactant; LAE-7.

Addition of N-ZnO increases the foamability of all tested surfactants (except for SDS at intermediate N-ZnO concentrations).

High concentrations of NS reduce the foamability of LAE-7, but improve the foam stability (in this contradiction the lack of SFP definition is clearly sensible).

In NS complemented fluids, CTAB foam has a higher stability than LAE-7 except for high NS concentrations.

N-ZnO decreases the CTAB foam stability considerably, especially in lowest tested concentration, but it shows a lower stability than LAE-7 foam in all concentrations.

In order to have a better foam selection, "Static Foam Performance (SFP)" has been defined here as;  $SFP = \int_0^{LDH} v_f dt \approx \sum_{i=1}^n A_i$  Using this definition, foamability and foam stability are considered simultaneously.

LAE-7 at low N-ZnO concentrations, CTAB at intermediate NS concentrations and LEA-7 at high NS concentrations have desirable SFPs, and the best selected foam in this method is not same as foamability and foam stability methods results.

Only high concentrations of NS have considerable effects on SFP of all surfactants and its effect on CTAB is absolutely lower and in a smaller range.

Due to the lack of applicability of SFP concept for previous works, a power correlation is developed in the form of;  $SFP = a \cdot FA^b \cdot FS^c$ , in which a, b and c are 0.6252, 0.9717 and 1.0486 respectively.

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