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Effect of Nanosilica on Critical Micelle Concentration of a Novel Sugarbased Surfactant -EOR Implication

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Abstract: Over 40% of the current world conventional oil production comes from carbonate reservoirs; dominantly mature and declining giant oilfields. After primary and secondary oil production stages using tertiary oil production methods as part of an Enhanced Oil Recovery (EOR) scheme is inevitable. Surfactant flooding aims at reducing the mobility ratio through lowering the interfacial tension between oil and water and mobilizing the residual oil. This article highlights the effect of nanosilica on critical micelle concentration of Zyziphus Spina Christi, a novel surfactant, in aqueous solutions for EOR and reservoir stimulation purposes. A conductivity technique was used to assess the critical micelle concentration (CMC) of the surfactant in aqueous phase. Electrical conductivity measured at 25°C. The influence of nanosilica concentrations on CMC variation of selected surfactant is considered. It was found the addition of nanosilica increase the CMC of surfactant decreases. Results from this study can help in appropriate selection of surfactants in design of EOR schemes and reservoir stimulation plans in carbonate reservoirs.

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1. Introduction

Carbonate rocks cover around 23% of the earth crust and contain as much as 50% of the world's proven conventional oil reserves and over 20% of the world's endowment of heavy oil, extra heavy oil and bitumen. More than 40% of current world oil production comes from Naturally Fractured Carbonate Reservoirs (NFCRs), dominantly mature and rapidly declining giant oilfields in the Middle East. Primary and secondary oil production stages result in Recovery Factors (RF) of commonly not greater than 0.45. Over 50% of the Oil Originally in Place (OOIP) is trapped in the reservoir rock as residual oil due to mobility issues and capillary barrier. Hence, to unlock this immense oil resource, implementation of tertiary oil production techniques as part of an Enhanced Oil Recovery (EOR) scheme is inevitable. However, chemical EOR methods were never responsible for a significant EOR oil production worldwide. Nevertheless, surfactants are increasingly used as a well stimulation or wettability alteration agents in EOR projects in carbonates and this is an active research area for the scientists around the world [1-10].

Surfactants are used in the presence of additives to improve their properties. Among the additives, alcohols are the most frequently used co-surfactants and many studies have examined the modulation of surfactant solutions by alcohols [11–16]. The effects of alcohols on surfactant solution properties, such as the critical micelle concentration (CMC) and micellar ionization degree, alcohol partition coefficient in micellar solutions, and micelle size and shape, have been reviewed [17-19]. The partitioning of alcohols and other additives in micellar solutions from CMC determinations has been studied by Treiner et al. [20-24]. Marangoni et al. [25, 26] determined the partitioning of alkanediols in SDS and DTAB micelles by NMR paramagnetic enhancement experiments and estimated the Gibbs energy of transfer from aqueous phase to the micellar phase. The energy decreases as the number of carbon atom in the alkanediol molecule increases.

2. Materials and procedure

2.1. Surfactant

Zyziphus Spina Christi is a tree with spiny branches and small commonly found in Jordan, Iran, Iraq, and Egypt. The concentration of saponins in Zyziphus Spina Christi is high [27]. Saponins are natural surface-active substances (surfactants) present in more than 500 plant species [28-29]. Their molecules include hydrophobic and hydrophilic parts. The hydrophobic part is composed of a triterpenoid or steroid backbone, and the hydrophilic consists of several saccharide residues, attached to the hydrophobic scaffold via glycoside bonds [30]. The combination of the nonpolar sapogenin and water-soluble side chain enables saponin to change to foam. Most synthetic surfactants having lipophilic and hydrophilic molecular parts have the same structure [27].

Three cyclopeptide alkaloids, as well as, four saponin glycosides, and several flavonoids can be extracted from the leaves of Zyziphus Spina Christi. Saponin which is a biosurfactant is produced from the leaves of Zyziphus Spina Christi. For the purpose of this study, the novel surfactant was extracted from the leaves by spray dryer method. The leaves of Zyziphus Spina Christi were collected from south of Iran and the saponin extracted by spray dryer method. The total extracted powder contains Saponin and Flavonoids. Powder has light brown color and soluble in water and alcohol. The density of the powder is 0.09 g/cm^3 and 1% of this powder in water has a pH of 5.9-6.0. Saponin is a natural and biodegradable nonionic surfactant. Properties of the novel surfactant is summarizes in Table 1.

Table 1: Properties of Zyziphus Spina Christi, a novel surfactant

Product	Total Extract Powder of Zyziphus Spina Christi
Used Part	Leaves
Preparation	Spray Drier
Description	Fine Powder
Color	Brown
Solubility in Cold Water	Soluble
Solubility in Alcohol	Soluble
pH value (10% Solution)	5.9-6.0
Density	0.09 g/cm^3
L.O.D at 110°c after 6h	1.6%-2%
Total Ash at 550°c after 4h	11.7%-12%
Applications	Medicine

2.2. Nanoparticles

The Nano silica in this study is a kind of modified ultra-fine powder, which is made from SiO2 and an additive. The shape of a nano particle looks like an approximate sphere when observed under a TEM. According to wettability of the surface of the silica nano particles, they can be classified into two types: hydrophilic silica nano particle (NSHI) and hydrophobic silica nano particle (NSHO). AEROSIL R 816 and AEROSIL 200 used as hydrophobic and hydrophilic nano particles which they were purchase from Degussa. Physical properties of AEROSIL R816 and AEROSIL 200 are shown in Table 2.

Table 1: Physical Properties of Nano Particles

	AEROSIL 200	AEROSIL R 816
Behavior with respect to water	Hydrophilic	Hydrophobic
Appearance	Fluffy white powder	Fluffy white powder
BET-Surface Area (m^2/g)	200±25	190±20
Average Primary Particle Size (nm)	12	12
Tapped Density (g/l)	50	40
SiO_2 (Wt%)	≥99.8	≥99.8
Al_2O_3 (Wt%)	≤0.05	≤0.05
Fe_2O_3 (Wt%)	≤0.01	≤0.01
TiO_2(Wt%)	≤0.03	≤0.03
HCl (Wt%)	≤0.025	≤0.025

2.3. Preparation of surfactant solution

The stock solution of Zyziphus Spina Christi with concentrations of between 1000 mg/L to 80000 mg/L were prepared by dissolving 0.10-8 g of Zyziphus Spina Christi in 1000 mL deionized water in a volumetric flask. These solutions were then diluted to obtain standard solutions containing 1000, 5000, 10000, 15000, 20000, 40000, 50000, 60000, 70000 and 80000 mg/L of the Zyziphus Spina Christi.

2.3.1. CMC measurement

There are several methods such as UV/Vis spectroscopy, voltametry, scattering techniques, calorimetry, surface tension and conductivity to measure the CMC. In this study, conductivity method was selected to carry out the CMC measurements. Concentration of the Zyziphus Spina Christi samples used was on the range of 1000-80000 ppm. Conductivity of the solutions was determined from high concentration to low. A Conductivity detector from the Crison Company was implemented in this research work. At first, the conductivity detector was calibrated by using a standard solution. In all of experiments electrode was washed up with distilled water and after that with peculiar solution. This is necessary to immerse probe of the conductivity meter in solution to guarantee the accuracy of solutions conductance. In the next step, conductivity in terms of concentration of Zyziphus Spina Christi was measured as shown in Figure 1.

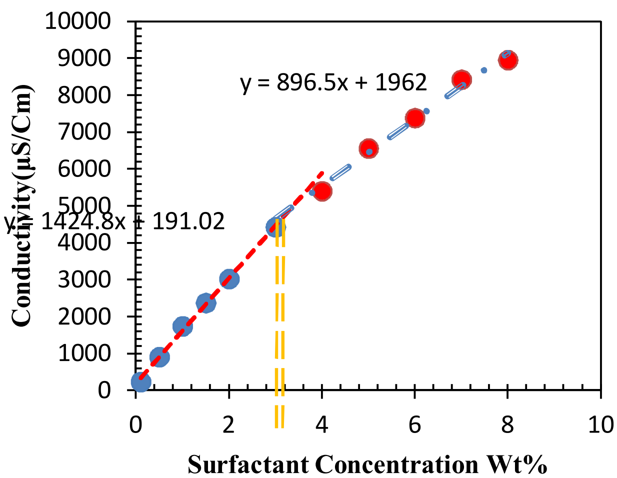

Figure 1: Conductivity vs. Surfactant concentration

3. Results and discussion

The changes in CMC with increasing the concentration of hydrophobic nanosilica are shown in Figs. 2–4. Intersection of two straight lines at a concentration that correspond to the Critical Micelle Concentration. This paper highlights micellization behavior of zyziphus spina christi in presence of different nanosilica such as hydrophilic nanosilica and partially hydrophobic nanosilica. Conductivity measurements revealed that at constant surfactant concentration, nanosilica presence, either hydrophilic or slightly hydrophobic, had a very small effect on solution conductivity as shown in Figure 5 for Zyziphus Spina Christi-AEROSIL 200/AEROSIL R816 systems. However, it seems that both nanoparticles influence the surfactant micellization properties particularly its critical micelle concentration. As it can be seen in Figure 5, co-existence of Zyziphus Spina Christi and AEROSIL 200 nanosilica in a solution leaded to a critical micelle concentration value lower that the one for sole zyziphus spina christi system. Figure 5 represents the critical micelle concentrations of different systems considered in this study, it can be seen that the presence of both nanoparticles have resulted in surfactant molecules to aggregate into micelles at lower concentrations. This phenomenon is more severe for higher nanoparticle concentrations.

The observed phenomenon may be related to surfactant-nanoparticle interactions. Ignoring the little amount of surfactant adsorption on nanoparticle surface, the similar negative electrical charge on the surfactant hydroxyl groups and nanoparticle surface results in an electrostatic repulsion between surfactant molecules toward each other and prompts the micellization process. Moreover, the hydrophilic nanoparticles make the bulk solution unfavorable for hydrophobic surfactant tails and increase their affinity to form micelles. Obviously, in such a situation, micelle aggregates form in lower concentration and critical micelle concentration is reduced, when nanoparticle concentration increase, the repulsion forces become stronger (due to larger number of nanoparticles). Also, the bulk solution becomes more hydrophilic. As a result, micellization occurs even at lower concentrations. Another important point that may be inferred from Figure 5 is that the dramatic reduction of CMC is more considerable for hydrophilic AEROSIL 200 nanoparticles. As it was mentioned before, the presence of these nanoparticles intensifies the hydrophilic characteristics of the solvent. As general rule, in aqueous medium, the greater the dissimilarity between the surfactant hydrophobic chain and solvent, the grater the aggregation number. Consequently, sharper decrease in CMC value is observed respect to AEROSIL R816 slightly hydrophobic nanoparticles.

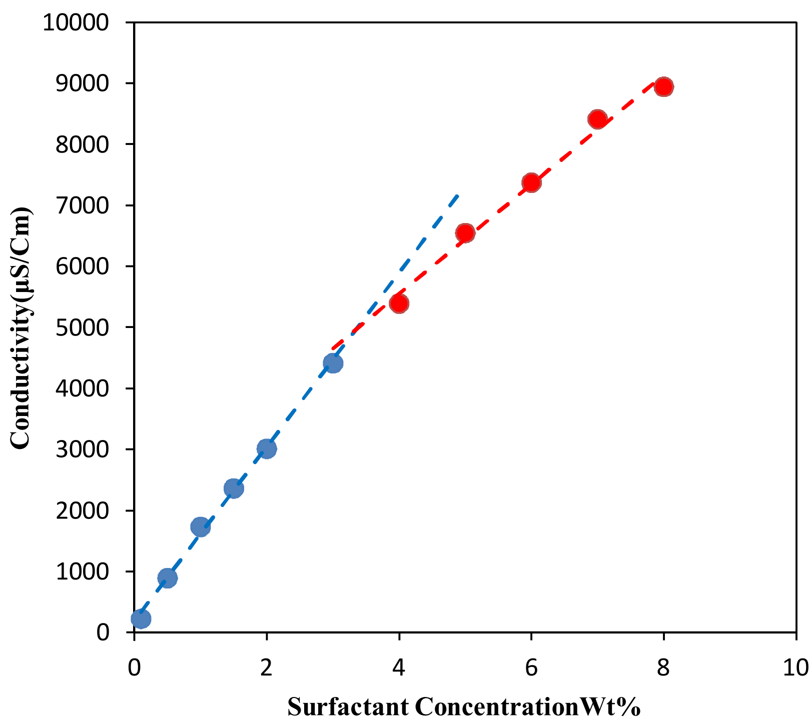

Figure 2: Effect of 500PPM of nanosilica On CMC of surfactant

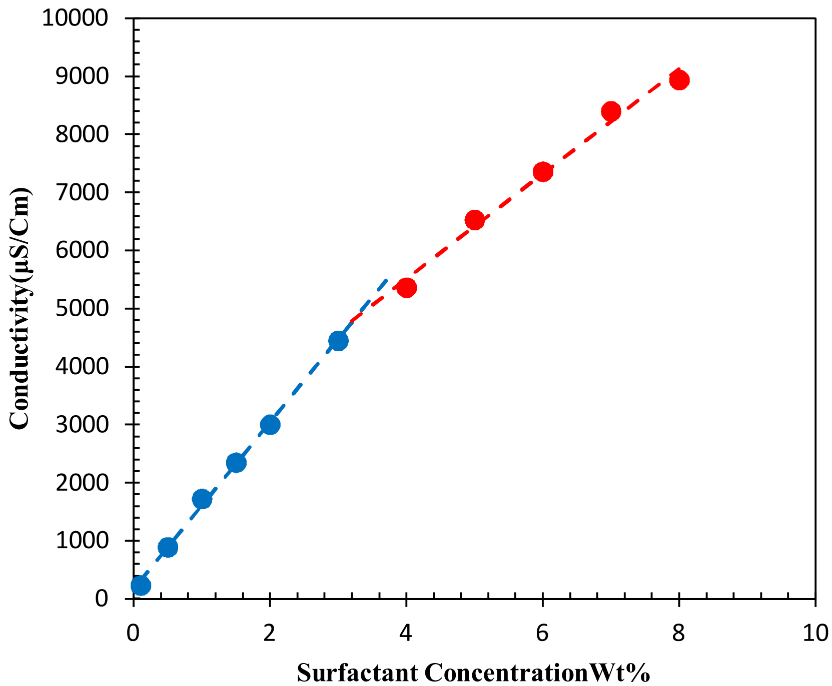

Figure 3: Effect of 1000PPM of nanosilica On CMC of surfactant

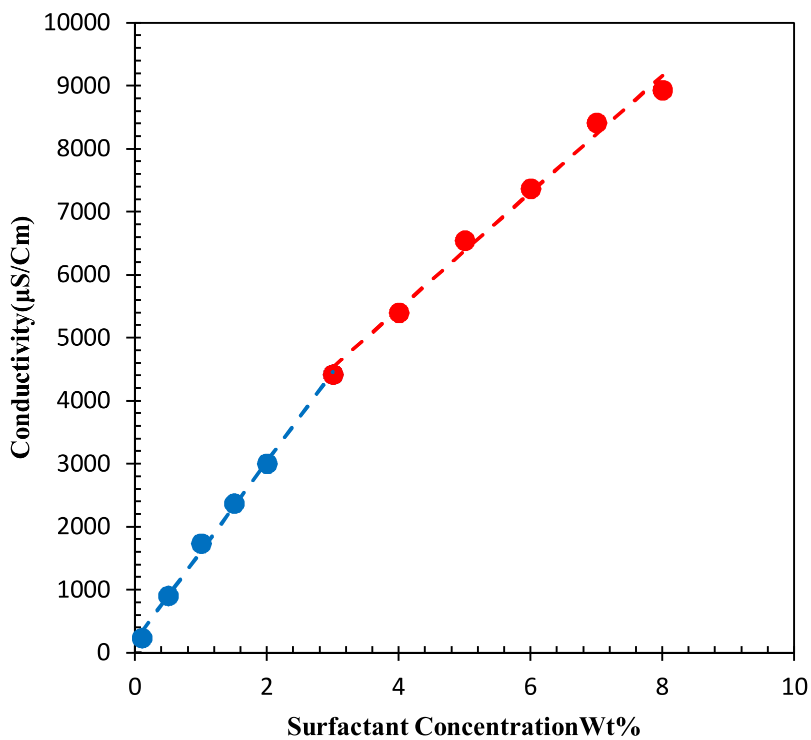

Figure 4: Effect of 2000PPM of nanosilica On CMC of surfactant

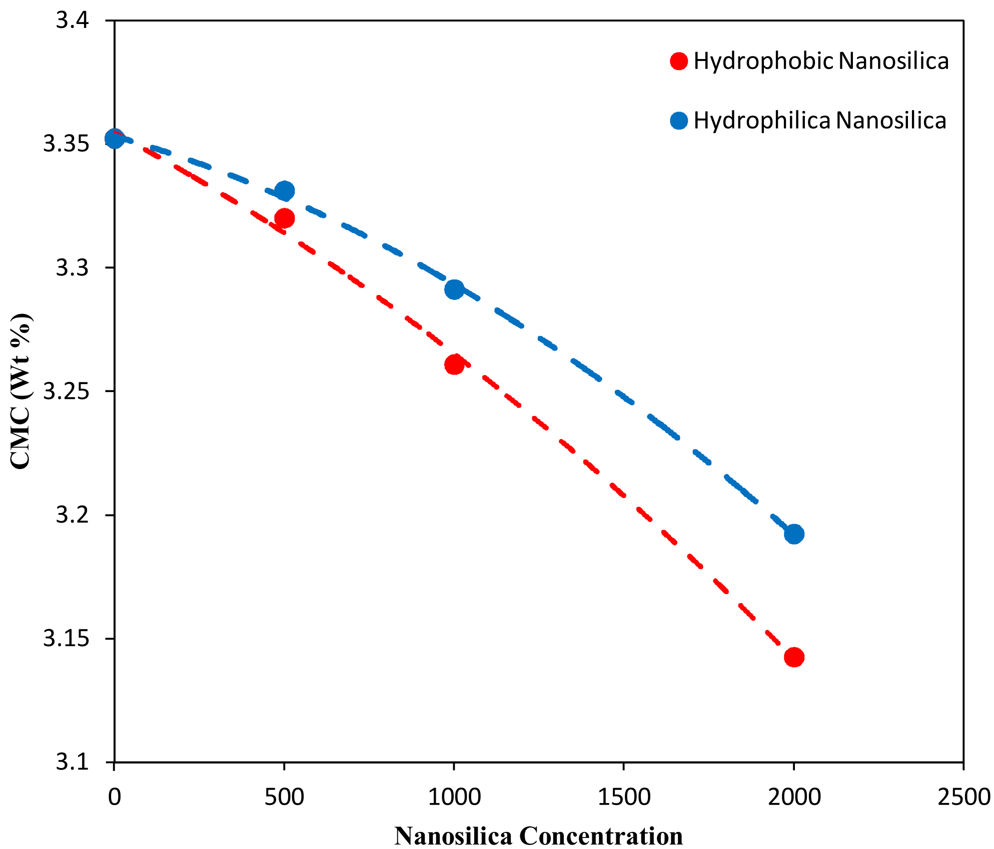

Figure5: Effect of Nanosilica on CMC value of Surfactant

4. Conclusions

In this work, effects of the addition of different nanosilica on the micellization and the micellar growth of Zyziphus Spina Christi in aqueous solution have been investigated. From results obtained from this work following conclusion can be drawn:

Ignoring the little amount of surfactant adsorption on nanoparticle surface, the similar negative electrical charge on the surfactant hydroxyl groups and nanoparticle surface results in an electrostatic repulsion between surfactant molecules toward each other and prompts the micellization process. In aqueous medium, the greater the dissimilarity between the surfactant hydrophobic chain and solvent, the grater the aggregation number. Consequently, sharper decrease in CMC value is observed respect to AEROSIL R816 slightly hydrophobic nanoparticles.

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