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Effects of Displacement Efficiency of Surfactant Flooding in High Salinity Reservoir: Interfacial Tension, Emulsification, Adsorption

Abstract: Surfactant could be used for enhancing oil recovery by enlarging displacement efficiency. The commercial anionic-nonionic polyoxyethylene alkyl sulfonate surfactants (ANS1 & ANS2) were used in high salinity reservoir(277g/L) and the performances were evaluated as well as the affect of salinity on performances in the range of 197g/L to 277g/L was studied. Interfacial tension was one of the most important factors. And the ultra interfacial tension could be obtained in the surfactant ANS1 concentration beyond 0.2% and ANS2 concentration beyond 0.3%. And interfacial tension had the trend of first decreasing and then increasing with increasing salinity. Emulsification can be represented by the unstability index (USI). The emulsification become better with increasing surfactant concentration and was not affected by salinity. The adsorption of surfactant on washed sands was much higher than that on oil sands. At the same time, with salinity increasing the adsorption increased. Displacement efficiency was not the result of single-factor, but was the representative of multi-factor of surfactant. It might be higher with ultra interfacial tension, better emulsification and lower adsorption.

Key words: Surfactant; Interfacial tension; Emulsification; Adsorption; Displacement efficiency; Salinity

1. INTRODUCTION

Surfactants were active substances used to reduce interface tension, which were amphiphilic compounds (containing hydrophilic and hydrophobic portions) that decrease the free energy through replacing the bulk molecules of higher energy at an interface. Cationic, anionic and nonionic surfactants can be used to enhance oil recovery (Mulligan C, 2001). Because of formation with negative electricity, the cationic surfactants can’t be used for flooding but can be used for sacrificial agents.

Surfactants flooding can enhance oil recovery by enlarging displacement efficiency (Hammond P, 2010, Shupe,RD1978, Carlin, JT1978). The primary requirement for mobilizing the residual oil was a sufficiently low interfacial tension (IFT), which makes the capillary number large enough to overcome the capillary forces and make the oil flow. There were many researches studied the effect of interfacial tension on displacement efficiency

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early(Wagner O.1966, Wade W.1978, Pingping Shen 2006). The researches indicated that observed increase in recovery could be obtained when the IFT was reduced to a value less than 0.07 mN/m. And some researches (Larson R.1978, Larson R.1979, Levitt D.2006) had studied the mechanism of surfactant flooding. Just the low IFT was not enough, due to the reservoir conditions, the best surfactant should satisfy other rigorous requirements. The requirements include the good ability of emulsifying oil, the low retention, thermal stability, wettability alteration, and low cost.

Emulsification was very important to enhance oil recovery, especially heavy oil recovery. After surfactant flooding, the reverse emulsion could obtain that reduced the viscosity of crude oil and changed the wettability. And oil recovery was increased through the mechanisms of oil entrapment and carrying by emulsification. Good emulsification could reduce the viscosity of crude oil and change wettability. Some researches (Wasan D.1978) had reported the effect of emulsification to displacement efficiency and how to get stable emulsion. Li (LI Jishan.2004) had studied emulsification by the method of the unstability index, which showed that emulsification was better with lower unstability index. And it was considered that the unstability index was qualitative relationship with interfacial tension. Yang F, Georgieva D, et al (Yang F, 2006, Georgieva D, 2009) had studied the influence factors of emulsion stability, including surfactant structure, the ratio of oil and water, the strength of interfacial film, and so on.

Low adsorption of surfactant could prolong the distance of flooding and enlarge the displacement efficiency. There were many studies reported adsorption of varies of surfactants on different surfaces (Hirasaki G, 1983, HirasakiG.J, 1982, Arpornpong N, 2007). Kang (Kang W, 2010) had studied the adsorption performance of surfactants used for combined chemical flooding, indicated that adsorption of surfactant was related with its lipophilicity and the saturated adsorption could be obtained near its critical micelle concentration. Wang (Wang Y.2002) had studied the adsorption of sodium dodecyl benzene sulfonate on washed sands and oil sands. Upadhyaya (Upadhyaya A.2007) had studied the adsorption of anionic-cationic surfactant mixtures on metal oxide surfaces, indicated that cationic surfactant could be observed to co-adsorb with anionic surfactant onto positively charged surface. And surfactant adsorption could be either enlarged or reduced by using mixed anionic-cationic surfactant system. Some researches (Puerto M. 1977, Hirasaki G, 1983, HirasakiG.J, 1982, Strand S, 2004) had studied the effect of salinity on adsorption. With salinity increasing, the saturated adsorption of anionic surfactant could increase.

In this paper, the performances of surfactants ANS1 and ANS2 had been studied under high salinity (277g/L), including interfacial tension, adsorption, emulsification and displacement efficiency. The effects of interfacial tension to emulsification and displacement efficiency, as well as the effect of interfacial tension, emulsification and adsorption to displacement efficiency, were studied under high salinity. At the same time, the changes of these performances with salinity were discussed at the range of 197g/L (the injection water salinity) to 277g/L (the original formation water salinity).

2. EXPERIMENTAL SECTION

Oil. The crude oil, which was from JiangHan oilfield in China, was dehydrated 12h at 85℃. The properties of the oil were as follows: density at 85℃, 0.869g/cm^3; viscosity at 85℃, 12.47mPa.s; asphaltenes content, 1.13wt%; gum level, 14wt%.

Tab. 1: Composition of the Different Brines at the Most Commonly Used Salinities

Ion	Concentration (mg/L)	
	The injection water	The original formation water
Na^+	75237.43	107318
Ca^{2+}	853.37	926.85
Mg^{2+}	192.06	106.4
Cl^-	115752.55	163956.25
SO_4^{2-}	3982.55	4262.66
HCO_3^-	448.47	442.4
Total dissolved solid(TDS)	197444.5	277012.56

Brines. The used synthetic brines were divided into two terms, the injection water and the original formation water. Their compositions were shown in table 1. And the density at 85℃ was that the injection water, 1.0692g/cm^3; the original formation water, 1.1289g/cm^3.

Porous media. The oil sands from JiangHan oilfield in China were ground into tiny grains, whose size distribution was in the range from 80 meshes to 200 meshes. In order to obtain the clean sands, a part of the oil sands was extracted 24h by toluene, and then dried in 85℃ oven. The property of the oil sands was the sandstone with the average oil saturate 35%.

Chemicals. The commercial anionic-nonionic polyoxyethylene alkyl sulfonate surfactants (ANS1 and ANS2) were provided from Chemical Institute of Shanghai, China. The purity was up to 90%.

IFT Measurements. The IFT measurements between the crude oil and the surfactant brines were performed at 85℃ by spinning drop interfacial tensiometer (Model Texas 500C). The IFT measurements were performed using the original formation water with different surfactant concentrations. Mix the injection water and the original formation water according to different proportions, and measure the IFT between oil and the mixed water with constant surfactant concentration 0.1wt% at 85℃.

Emulsification. The emulsification experiments were performed in 10mL stoppered test tube scale with 5mL crude oil and 5mL surfactant solution. After sealed and preheated to 85℃, the test tube was oscillated up and down evenly, then put vertically into the 85℃ thermostat water bath at once. At the same time start time and record the water volume separated of the test tube at the interval of 1min in the next 1hour. The unstability index (USI), which was calculated by the curve of the relationship between separated water volume and time, could be used to represent the emulsification.

$$USI = \frac{\int_0^t V(t)d_t}{t}$$

Where USI was the unstabiity index, $\int_0^t V(t)d_t$ was the function between separated water ratio and time, t was the separated time. Change the salinity of the water by mixing the injection water and the original formation water according to different proportions. And the effect of salinity to emulsification was observed.

Adsorption. The adsorption experiments were performed with a 250mL stoppered conical flask with 75mL surfactant solution and 25g oil sands, containing the ratio of solution to sands(SSR) was equal to 3. After that, put the stoppered conical flask on the 85℃ stable temperature horizontal shaking bath 24h. Then centrifuged and measured the concentration of the surfactant solution with the 754 UV visible spectrophotometer. The adsorption could be calculated with the following formula:

$$\Gamma = G(G_0 - G_e)/M$$

Where Γ was the adsorption, G was the total volume of surfactant solution, G_0 was the initial concentration of the surfactant solution, G_e was the balance concentration of the surfactant solution after adsorption, M was the quality of oil sands. At the same time, the effect of SSR and salinity was evaluated.

Displacement Efficiency (DE). The DE experiments were carried with extracted oil sands, whose size distribution was in the range from 80 to 100 meshes. After extracted cleanly by toluene, the oil sands were saturated with Jianghan crude oil and aged at 85℃ oven 10days. During this period, the oil sands were stirred at intervals in order to be saturated evenly. The mixture of the prepared oil sands and 0.1wt% surfactant solution in certain proportion was put into a stoppered conical flask and carried on the 85℃ stable temperature horizontal shaking bath 48h. The concentration of crude oil in surfactant solution was measured by the 754 UV visible spectrophotometer at the wavelength of 339nm. At the same time, the prepared oil sands were washed completely with petroleum ether and measure the total quality of crude oil attached on the oil sands. Therefore, the DE was equal to the ratio of the quality of crude oil in surfactant solution to the total quality of crude oil attached on the oil sands. At the same time, the effect of surfactant concentration and salinity was evaluated.

3. RESULTS AND DISCUSSION

IFT Measurements. The results of IFT between crude oil and surfactant aqueous solution were shown in fig.1. It indicated that the surfactant ANS1 could reduce IFT more efficiently than surfactant ANS2. With low surfactant ANS1 concentration, the IFT between crude oil and aqueous solution could reach an ultraslow value. When the concentration of surfactant ANS1 was 0.3wt%, the IFT decreased to the lowest value. Before the micelles forming, the hydrophobic groups were transferred to the interface between oil and water from the surfactant aqueous solution, which resulted in the IFT decreased. After the micelles forming in aqueous solution, the effective surfactant concentration was reduced by the solubilization of micelles. Therefore, the quantity of surfactant molecular exited in the oil- water interface was reduced, that leaded the IFT to increase.

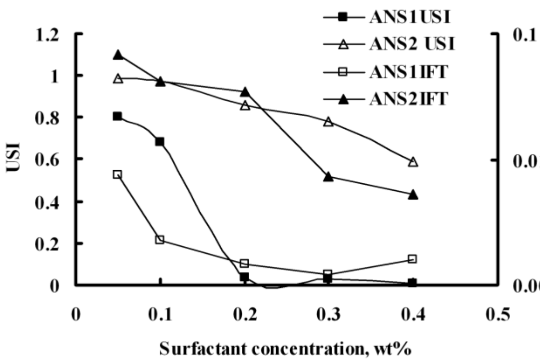

Fig. 1: The Change of IFT and Emulsification with the Concentration of Surfactant at 85℃

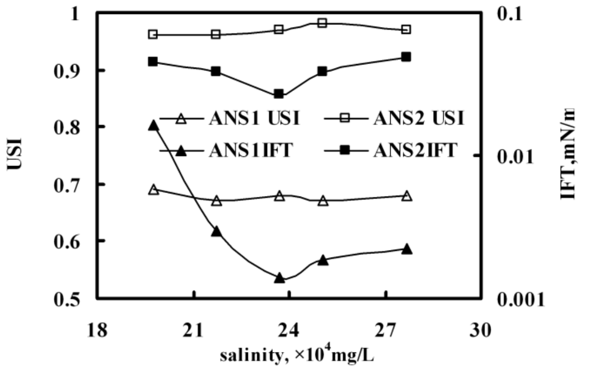

Fig. 2: The Effect of Salinity on IFT and USI with 0.1 wt% Surfactant at 85℃

The effect of salinity on IFT was investigated, as shown in fig.2. With salinity increasing the IFT presented the trend of first decreasing and then increasing marginally with increasing salinity. The lowest IFT of ANS1 and ANS2 were obtained at the salinity value of 23.72×10^4mg/L. At low concentration of salinity, almost surfactant molecules existed in formation water. And the surfactant molecules gradually transferred from formation water to the crude oil, which made the IFT drop. The IFT would attain the lowest at the special concentration of salinity when the concentration of surfactant in formation water was equal to that in crude oil and the partition coefficient approached 1. Adding sodium chloride into the ionic surfactant solution not only shielded the ionic charge and compressed the thickness of the surfactant ion layer, but also destroyed the hydration shell around the hydrophilic groups and constrained water affinity of surfactant. These made the surfactant molecules adsorb on the intension face easily and decrease the IFT. But the IFT would increase with concentration of sodium chloride further increasing when most surfactant molecules existed in crude oil and the adsorption equilibrium between the formation water and crude oil was destroyed.

Emulsification. The unstability index (USI) could be used to represent the stability of emulsion. The smaller the USI was, the better the emulsification was. The emulsification of ANS1 was better than that of ANS2 at the same conditions, as shown in fig.1. Furthermore, the emulsification of them became better with increasing concentrations. And the emulsification of surfactant was intimately connected with the IFT which was an important factor affecting the emulsification. From fig.1, Both ANS1 and ANS2 had the same trend which was that the emulsification was inclined to become better with decreasing IFT. But not all of surfactants had this objective law. This was because there were many factors affecting the emulsification, such as the strength of interfacial film, the properties of surfactants, and so on. And the effect of salinity on IFT was different from that on emulsification. The effect of salinity on emulsification could be negligible, but it had an important role on IFT.

Adsorption. In oil field, the injected surfactant was used to reduce the IFT between crude oil and formation water, then enlarge displacement efficiency and enhance oil recovery. If the interaction between surfactant and the porous media was strong, the concentration of surfactant would decrease sharply along the flow direction and the operation distance of surfactant was not long enough to satisfy the needs of operation. So if possible, the surfactant which had light adsorption might be selected to be used in oilfield. From fig.3, the standard adsorption curve was obtained. The results showed that the ANS1's absorbance change of gradient with concentration was smaller than that of ANS2's. From fig.4, the results of adsorption on washed sands and oil sands were obtained, shown that the equilibrium adsorption on washed sands was much bigger than that on oil sands. The equilibrium adsorption of ANS1 was much lower than that of ANS2. The equilibrium adsorptions of both ANS1 and ANS2 increased with increasing concentrations of surfactants. On the surface of the oil sands, there were many kinds and quantities of organic substances and polar materials, even including some surface active substances existing in crude oil，which had occupied on oil sands and decreased the surfactant adsorption on oil sands. At the same time, the crude oil adsorbed by surfactant might blend in surfactant solution through emulsification or solubilization, which might make the concentration of surfactant solution increase. This phenomenon could be confirmed by the colour of surfactant solution after being adsorbed. The colour of surfactant solution after being adsorbed by oil sands was brown, but colorless after being adsorbed by washed sands. With surfactant concentration increasing, the equilibrium adsorption always increased and much bigger than normal value. So if these two surfactants were used in oilfield, sacrificial agents must be used first in order to reduce surfactant adsorption. Under surfactant solution, the surface of washed sands was electronegative and formed electric double layer. The electricity of both washed sands and surfactant was reduced by injected salts that leaded to the repulsive force between them. So with salinity increasing, the equilibrium adsorption increased.

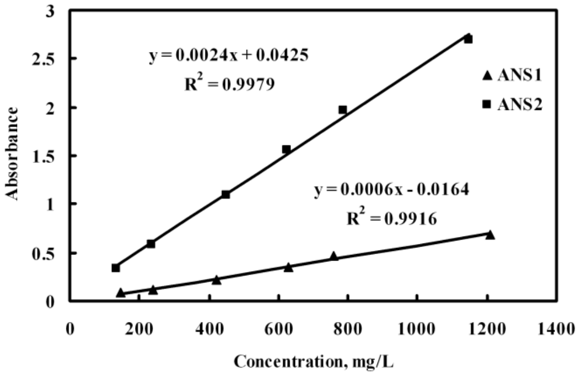

Fig. 3: The Standard Adsorption Curve

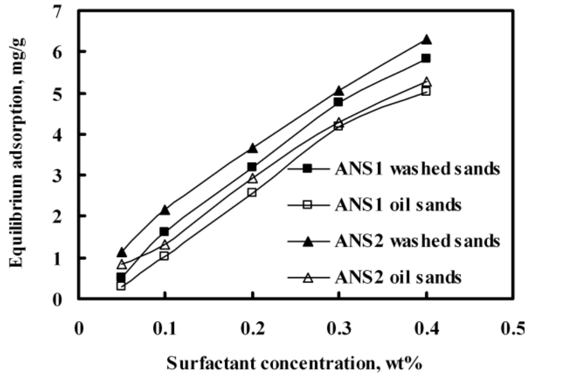

Fig. 4: The Change of Equilibrium Adsorption with Surfactant Concentration

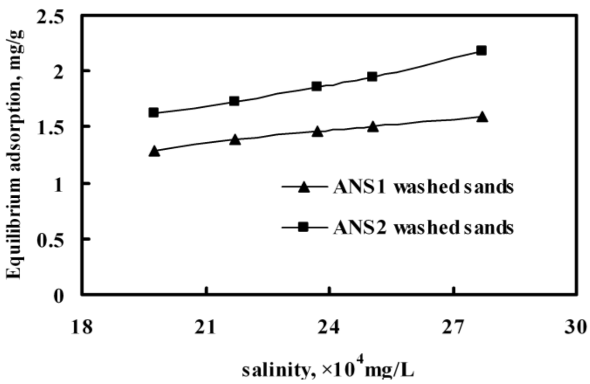

Fig. 5: The Effect of Salinity on Adsorption with 0.1 wt% Surfactant at 85℃

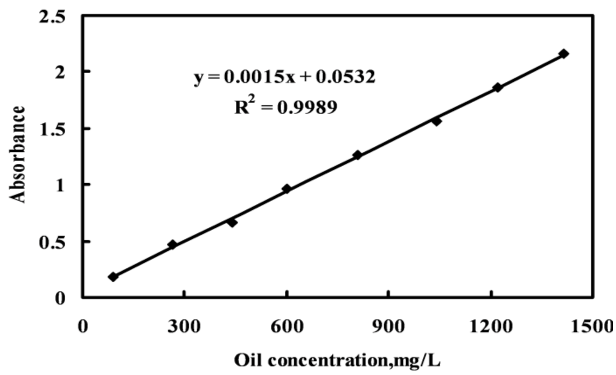

Fig. 6: The Standard Curve of Oil Absorbance

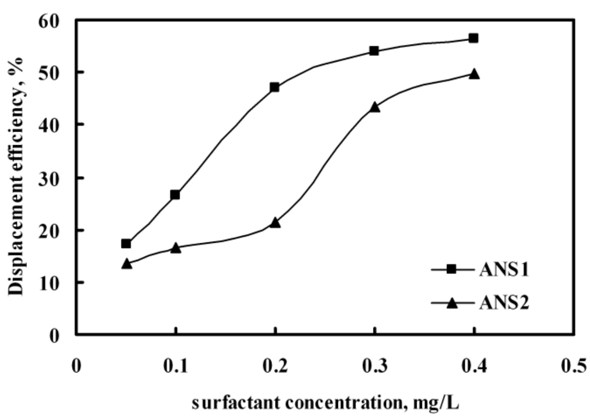

Fig. 7: The Change of Displacement Efficiency Concentration of Surfactant at 85℃

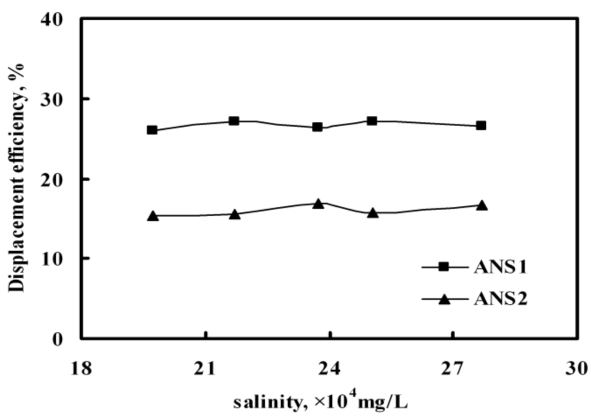

Fig. 8: The Effect of Salinity on with the Displacement Efficiency with 0.1 wt% surfactant at 85℃

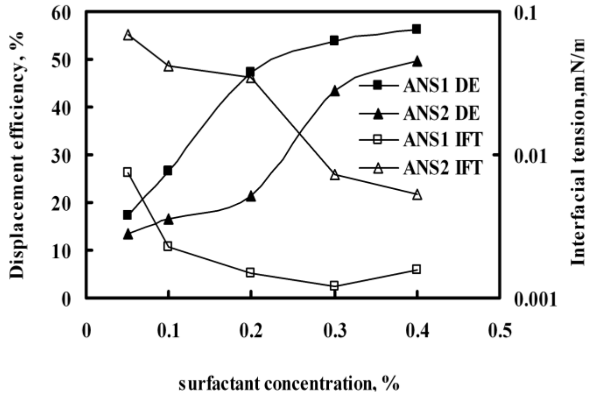

Fig. 9: The Change of Displacement Efficiency with Interfacial Tension under Different Surfactant Concentration at 85℃

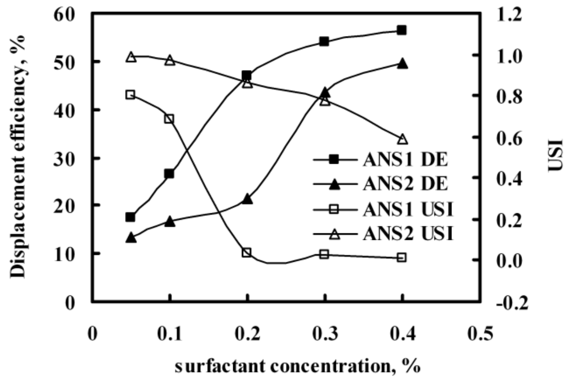

Fig. 10: The Change of Displacement Efficiency with Emulsification under Different Surfactant Concentration at 85℃

Displacement Efficiency (DE). Displacement efficiency was one of the most important standards to measure the performance of surfactant. There were many factors affecting displacement efficiency, such as interfacial tension, emulsification, adsorption, and so on. The results of displacement efficiency were indicated that with increasing surfactant concentration, displacement efficiency of both ANS1 and ANS2 increased. And ANS1's displacement efficiency was much better than that of ANS2, especially under low surfactant concentration, shown in fig.7. From fig.8, displacement efficiency remained unchanged with increasing salinity with the surfactant concentration at 0.1 wt%. With interfacial tension decreasing, the displacement efficiency increased, especially at high concentration (more than 0.2 wt%). The displacement efficiency remained constant when the interfacial tension was below 10^{-3} mN/m order of magnitude. When surfactant concentration was 0.2 wt%, ANS1's interfacial tension was 1.47×10^{-3}mN/m, but ANS2's was 3.43×10^{-3}mN/m. And the displacement efficiencies of ANS1 and ANS2 were 47.08%, 21.4%. It indicated that interfacial tension was one of the most important factors those affected displacement efficiency. And when surfactant concentration was 0.1 wt%, ANS1's interfacial tension was much lower than that of ANS2. But the difference of displacement efficiencies between them was little. It showed that interfacial tension was not the only factor affecting displacement efficiency. The relationship between displacement efficiency and emulsification was shown in fig.10, showed that the better emulsification was, the better displacement efficiency was. So the difference of interfacial tension between ANS1 and ANS2 was obvious, but the difference of emulsification was little. That might be why the difference of displacement efficiency between ANS1 and ANS2 at 0.1 wt% was little. When interfacial tension and emulsification had not been changed with increasing concentration, for example ANS1 at 0.2%, 0.3% and 0.4%, displacement efficiency also changed a little. And if the bigger adsorption was, the lower the equilibrium concentration in surfactant solution was. Displacement efficiency was affected by adsorption by being reduced the surfactant concentration. To sum up, displacement efficiency was not the result of single-factor, but was the representative of multi-factor of surfactant.

4. CONCLUSION

a. In high salinity reservoir (270g/L), the ultra interfacial tension between crude oil and formation water could be obtained by using the surfactant ANS1 and ANS2. And interfacial tension had the trend of first decreasing and then increasing with increasing salinity in the range of 197g/L to 277g/L.

b. The emulsification can be represented by the unstability index. The smaller the unstability index was, the better the emulsification was. The low unstability index could be obtained by using the surfactant ANS1 at the concentration beyond 0.2 wt%. And the emulsification was not affected by salinity in the range of 197g/L to 277g/L.

c. The adsorptions of ANS1 and ANS2 were much higher than normal. The adsorption on washed sands was much higher than that on oil sands. And with salinity increasing in the range of 197g/L to 277g/L, the adsorption increased.

d. Displacement efficiency was affected by interfacial tension, emulsification and adsorption, but not affected by salinity in the range of 197g/L to 277g/L. displacement efficiency might be high with ultra interfacial tension, good emulsification and low adsorption.

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