EFFECT OF NaCl IN CLOUD POINT OF NONIONIC SURFACTANTS AND ADSORPTION BEHAVIOR FOR CHEMICAL FLOODING IN ENHANCED OIL RECOVERY

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ABSTRACT

Surfactants are widely used in enhanced oil recovery, due to its chemical properties, like reduction of the interfacial tension between two immiscible liquids. For nonionic surfactants, the cloud temperature is an aspect important to be evaluated, since above this temperature an initially homogenous surfactant solution separates into two phases, losing their proprieties. This work evaluates cloud temperature, critical micelle concentration and adsorption for solutions of nonionic surfactant with different concentrations of NaCl, used in enhanced oil recovery. Nonionic surfactants polyoxyethylene (20) sorbitan monolaurate (T20), polyoxyethylene (20) sorbitan monooleate (T80), octylphenol ethoxylate with 10 moles of ethylene oxide (TX100), and Nonylphenol polyoxyethylene with 15 moles of ethylene oxide (U150) were used. From results obtained, it was observed that cloud points varied considerably for surfactants studied and, also, with different NaCl concentrations. Was observed that for the surfactants studied, except for the TX100, cloud point temperatures exhibited values above the average temperature of oil wells (~55 oC).It means that these surfactants can be used for oil recovery, significantly broadens the scope of application for conventional chemical EOR methods, getting good recovery results and without large losses of surfactant by adsorption amount (0,08 g surfactant/g sandstone), making the process more efficient.

INTRODUCTION

Surfactants are amphiphilic molecules composed of two parts, one hydrophobic and the other hydrophilic. Aqueous solution of surfactants, especially micelles, are solutions that depend on surfactant concentration. At concentrations above the critical micelle concentration (CMC), they form aggregates known as micelles, where the hydrophobic tails flock to the interior while the hydrophilic heads remain on the outer surface so as to minimize and maximize their contact with water, respectively (Israelachvili, 1992; Tanford, 1980 and Chevalier, 1990). Surfactants, however, are subject to changes in their properties through variations in temperature and pressure. The solubility of surfactants, for example, varies greatly with temperature; ionic surfactants tend to have increased solubility

related to a higher temperature, while the nonionic tend to be less soluble at elevated temperatures. The solubility reduction feature is a limiting factor for the use of nonionic surfactants, either because of esthetic effects (cloudiness or phase separation) or because their surfactant functions are reduced at higher temperatures (Daltin, 2011). When the temperature increases, at a certain point, the behavior of an aqueous micelle solution of nonionic surfactant also changes, so that a cloud of insoluble surfactant appears in the solution. Critical micelle concentration (CMC) is an intrinsic characteristic of any surfactant. The CMC is the lowest concentration at which there is formation of micelles (micellization) and when the surfactant shows some changes in characteristics such as in surface tension, turbidity, molar conductivity, pH, viscosity, light scattering, osmotic pressure and solubilizing capacity. At a certain temperature, a single-phase surfactant micelle aqueous solution, for example, separates into a dilute phase and a coacervate phase. The temperature at which phase

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separation occurs is known as cloud point, as it is characterized by an increased cloudiness of the solution which can be observed visually (Akbas, 2009 and Batıgöc, 2011). In addition, the increase of salt concentration in nonionic surfactant solutions causes variations considerably in cloud point, since it reduces the solubility of the surfactant in water (Santos-Ebinuma, 2013 and Curbelo, 2008). These systems have been used in oil recovery (Curbelo, 2008; Curbelo, 2013 and Howe, 2015). Oil, when found in nature, is present in the pores of rocks, known as reservoir rocks. Only a fraction of the oil present in these reservoirs, however, can be extracted. Remaining tapped in the rock, great fraction of the oil. Oil production is thus reduced, not only by the decrease in the volume of oil in the well, but also by changes in physicochemical properties such as viscosity and density, which occur over time (Thomas, 2004). Thus, the development of advanced methodologies to optimize the recovery of remaining oil is critical in extending the useful life of wells and making them economically viable for exploration. Conventional oil recovery methods, where there is no chemical and thermodynamic interaction between fluids or between the fluid and rock, are generally less efficient. Advanced oil recovery techniques, called Enhanced oil recovery (EOR), are used in places where conventional oil recovery methods have failed or would fail if they were used.

EOR methods are classified into Thermal, Miscible and Chemical methods, according to general nature of the processes. Among these methods, Chemical Methods, which propose a certain chemical interaction between the injected fluid and reservoir fluid, have proven very effective with respect to the percentage of oil recovered (Park, 2014). In regard to chemical methods, a useful technique is through the injection of surfactant solutions (Park, 2015). Surfactants can reduce interfacial tension between water and oil, increasing displacement efficiency and removing oil, thus causing an increase in the oil recovery factor (Curbelo, 2008 and Park, 2014). In this study, critical micelle concentration, cloud point and adsorption of nonionic surfactants, Tween 20 (T20), Tween 80 (T80), Triton X-100 (TX100) and Ultranex NP150 (U150), were investigated in variations of salt concentration (2%, 5%, 10%, 15%wt NaCl) in surfactant solutions. The NaCl was chosen due to its higher concentration in produced water (brine) of oil reservoirs and more interference on surfactant properties used in enhanced oil recovery.

MATERIALS AND METHODS

Surfactants: Four nonionic surfactants were studied: polyoxyethylene (20) sorbitanmonolaurate (T20), polyoxyethylene (20) sorbitanmonooleate (T80), octylphenolethoxylate with 10 moles of ethylene oxide (TX100), and nonylphenolpolyoxyethylene with 15 moles of ethylene oxide (U150). The surfactants T20, TX100 and U150 were obtained from Oxiteno (Brazil) and T80 was obtained from Dinâmica Química ContemporâneaLtda, Brazil, they were used as received, without any purification.The saline solutions (brine) were prepared with concentrations of 2%, 5%, 10% and 15% wt of NaCl.

Critical micelle concentration: Surface tensions of the surfactant solutions at different concentrations were determined at 25º C using a Surface Tensiometer (Sensa Dyne Instrument Div). The break in the plots of ln concentration versus surface tensions corresponds to CMC value.

Cloud point: The temperature corresponding to cloud point was verified visually, by the change of solution turbidity when the sample was heated at a rate of about 1ºC/min until it reached the cloud point temperature. The solutions were stirred and heated with a magnetic stirrer with temperature control (Figure 1).
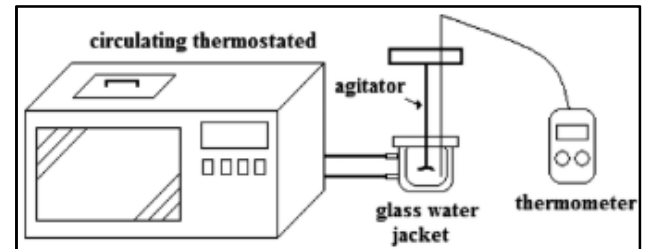

Fig. 1. System used to determine cloud point

Adsorption: For the determination of the equilibrium time, samples comprising adsorbent with volumes of surfactant solution (60 mL), with concentration of 0.015 g/L until 3.0 g/L, were stirred with a Dubnoff Shake, at a temperature of 28ºC, during 3 hours. The equilibrium time was established when the solution concentration no longer varied. The result obtained of granulated group of adsorbent (rock) of the greater percentage (~61 %) was for the –65+250 # group. The adsorbed amount (q) was calculated by a simple mass balance between the initial and final solution conditions, represented mathematically by Equation 1.

$$q = \frac{V(C_0 - C_e)}{m}$$ ……………….(1)

Where: C_0 and C_e are initial and equilibrium concentrations of surfactant (mg/L) respectively, V is volume of surfactant solution (L), m is mass (g) and q is the surfactant amount adsorbed on adsorbent (mg/g).

RESULTS AND DISCUSSION

Critical micelle concentration (CMC): The determination of the CMC is of fundamental importance to any procedure involving surfactants since the effects of these compounds are increased when a significant amount of micelle is present. Figures 2to 5 show the results for the CMC of the nonionic surfactants studied, in different salt concentrations.
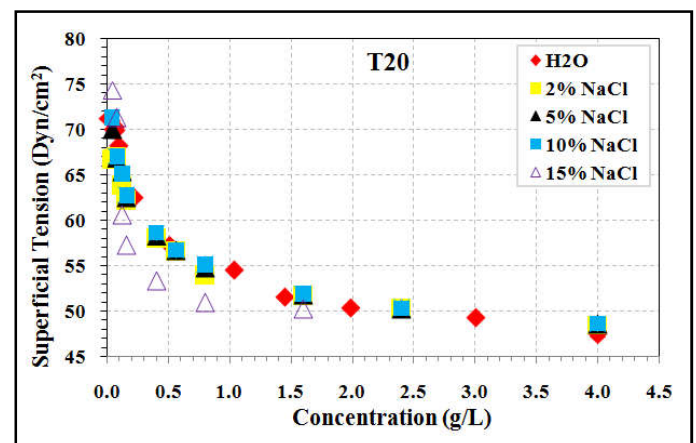

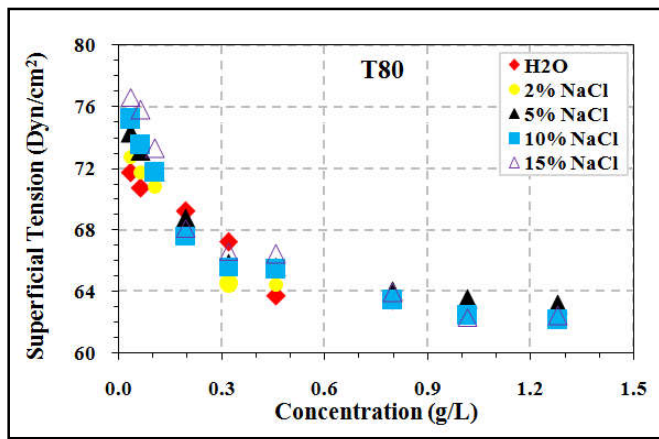**Fig. 2. CMC of T20 in water and different salt concentrations**

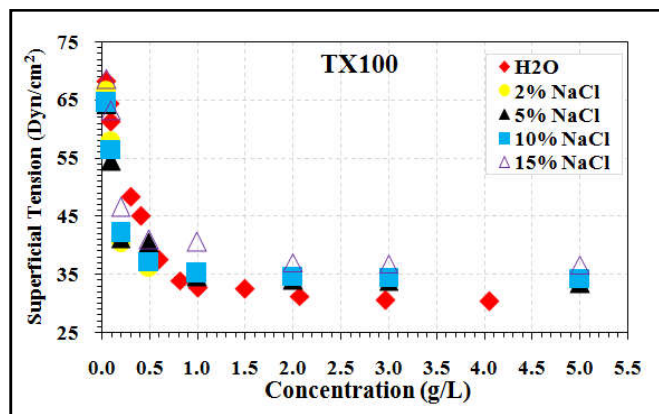**Fig. 3. CMC of T80 in water and different salt concentrations**

Fig. 4. CMC of TX100 in water and different salt concentrations
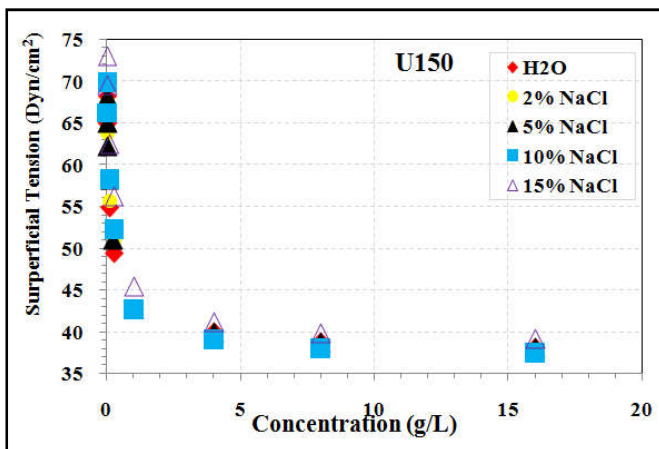

Fig. 5. CMC of U150 in water and different salt concentrations

As shown in Figures 2-5, it is observed a decrease in the interfacial tension when the concentration of the surfactant increases. In sequence, there is a time in which the curve starts to become constant, which means that the surfactant can no longer adsorb in the interface and begin to form micelles. At this point, there is the CMC. Observing the Table 1, it is verified that EO unit is responsible for the hydrophilic part of the chain; the larger the EO chain, the more soluble the molecule is in the water, therefore, the greater should be the value of the CMC, since it would take more molecules to form micelles.

Table 1. Surfactant characteristics

Surfactant	Molecular Weight (g/mol)	HBL
T20	1228	16.7
T80	1310	15.0
TX100	625	13.5
U150	881	15.0

Surfactant T20 is chemically known as polyoxyethylene sorbitan monolaurate and T80 as polyoxyethylene sorbitan monooleate. Both surfactants have the same polar group and differ only in the side chain structures of the fatty acids. The EO value for both surfactants are 20, however, comparing HBL values and knowing that the smaller the HBL (Table 1), the more lipophilic the molecule, therefore T80 is less soluble in water than T20, and T80 forms CMC in lower concentrations (3.47×10^{-5}mol/L) than in T20 (5.47×10^{-5}mol/L). The difference is not so great, due to the fact that they have the same number of EO and because the difference between their HBL is not so great (Figures 2 and 3). As for surfactants TX100 and U150 (Figures 4 and 5), there is a pronounced difference in their CMC. The TX100 has a lower CMC (9.28×10^{-4}mol/L) than U150 (1.44×10^{-3}mol/L). However, there isn't any parameter which can explain the relationship between their CMC, once they are derived from different chains.

Cloud point: Figures 6 to 9 show the effects of salt concentration on the cloud point of surfactants. Increasing salt concentration reduces the turbidity temperature (cloud point) of the surfactant solution, for all the nonionic surfactants studied.
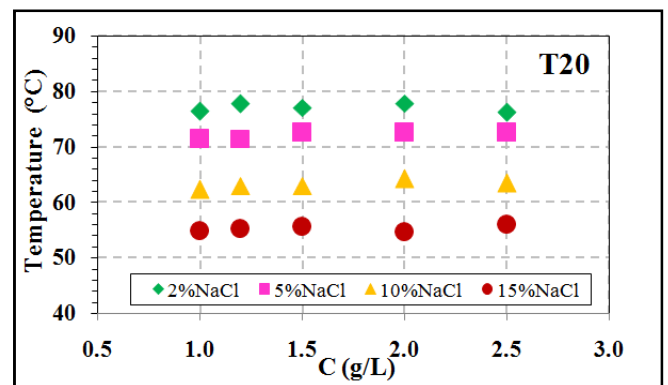

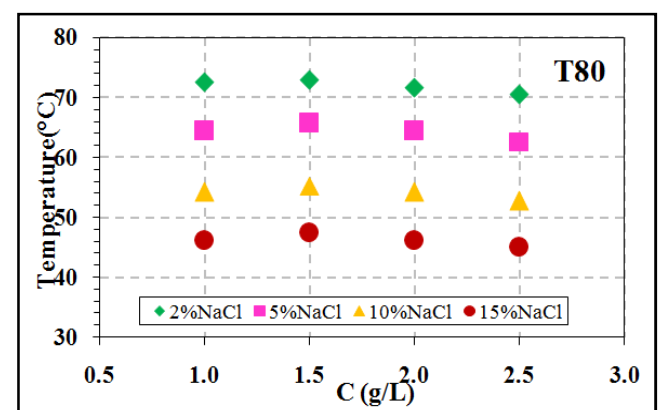**Fig. 6. Cloud point temperature of T20 at 2%, 5%, 10% and 15% NaCl concentration**

Fig. 7. Cloud point temperature of T80 at 2%, 5%, 10% and 15% NaCl concentration

For the surfactants T20 and T80 (Figures 6 and 7, respectively), a decrease in cloud point with increasing nonpolar chain was observed (Table 2), such as for 15 % NaCl, average temperature of 55.2 °C was observed for T20, whereas for T80 average temperature was 50.4 °C. The same was observed for the other concentrations of salt. Below the cloud temperature (below each curve), only one liquid phase

exists, micelle phase, whereas in the region above of this temperature, two coexisting liquid phases are found, a surfactant rich phase (coacervate phase) and a water phase (dilute phase).

Fig. 8 Cloud point temperature of U150 at 2%, 5%, 10% and 15% NaCl concentration

Fig. 9. Cloud point temperature of TX100 at 2%, 5%, 10% and 15% NaCl concentration

For use of a particular surfactant in enhanced oil recovery, when the surfactant solution reaches cloud point, the coacervate phase can be deposited (adsorbed) in the rock. With adsorption, there is a reduction of surfactants in the solution, reaching a concentration value below the CMC, thus decreasing oil recovery efficiency. Results cloud point temperatures show a linear relationship when the salt concentration increases. The higher salt concentrations lead to lower cloud points. The variations in cloud point followed the behavior decreasing: U150 > T20 > T80> TX10 (Table 2). This was due to differences in nonpolar chains of the surfactants, which is characteristic of each surfactant.

Table 2. Cloud temperature of surfactants with variations of NaCl concentration

Surfactant	2%wt NaCl	5%wt NaCl	10%wt NaCl	15%wt NaCl
T20	77.7°C	71.9°C	63.2°C	55.2°C
T80	71.9°C	64.3°C	54.1°C	46.2°C
U150	89.9°C	80.0°C	78.8°C	67.6°C
TX-100	58.6°C	50.9°C	40.0°C	31.6°C

The results of this study show that the salt concentrations (2, 5, 10, 15 wt% NaCl) and surfactants studied, except Triton X-100 formed cloud points temperatures above the average temperature of oil wells.

Adsorption

From the surfactants studied, it is observed that U150 has great potential to be used in EOR, because its cloud point temperatures, for all salinities studied (2, 5, 10 and 15% NaCl), are above the temperature average oil wells (~ 55 ^{o}C). Thus, the study of the adsorption of this surfactant in the rock was done to obtain the amount of adsorbed surfactant and to verify if the process may or may not be viable. Figure 10 shows adsorption of U150 in sandstone.
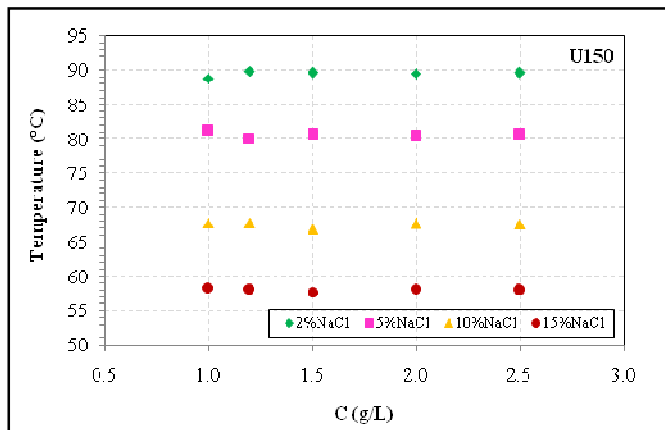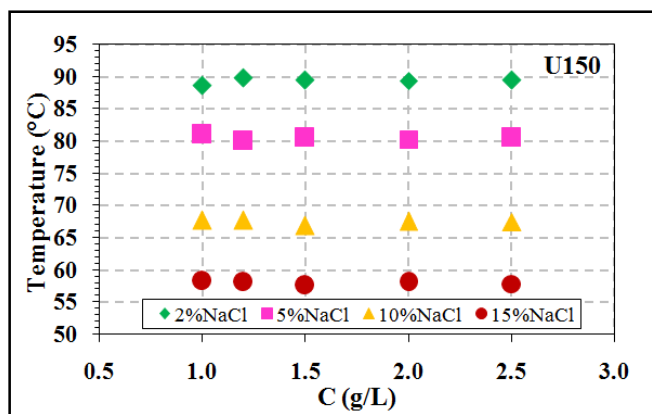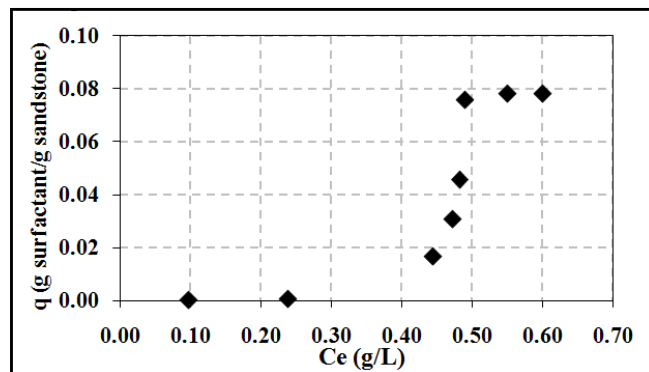

Fig. 10. Adsorption isotherm for surfactant U150

The results obtained for U150 indicated that adsorption is unfavorable, due to low surfactant adsorption in the rock, presenting very weak interactions, because adsorbent-adsorbate (sandstone-surfactant) interactions are weaker than the adsorbate-adsorbate (surfactant-surfactant) and adsorbent solvent. The low adsorption amount 0,08 g surfactant/g sandstone exerted by the surfactant U150 on the rock shows a satisfactory result for its use in EOR.

Conclusion

In this work, it was verified that of the four surfactants studied, only two (T20 and U150) can be effective in EOR methods, because under high salinity conditions, cloud point temperatures are above the average oil wells temperatures (~ 55 °C). This means that they can be used for oil recovery ensuring satisfactory recovery without losses of surfactant by adsorption, observed by U150, making the process viable and very efficient. Thus, the importance of knowing the behavior of these surfactants solutions in the presence of salts prior to employ them for oil industry.

Acknowledgements

REFERENCES

Akbas, H. and Batıgöc, C. Spectrometric studies on the cloud points of Triton X-405, 2009; 279:115-119.doi: 10.1016/j.fluid.2009.02.014.

Batıgöc, C. and Akbas, H. Spectrophotometric determination of cloud point of Brij 35 nonionic surfactant. 2011; 303: 91-95.doi: 10.1016/j.fluid.2011.01.004.

Chevalier, Y. and Zembf, T.The structure of micelles and microemulsions. Reportson Progress in Physics, 1990;53, No. 3, 279.doi: 10.1088/0034-4885/53/3/002

Curbelo, F. D. S., Barros Neto, E. L., Dutra Junior, T. V., Castro Dantas, T. N., and Garnica, A. I. C. Oil recovery performance of surfactant solutions and adsorption in sandstone. *Petroleum Science and Technology.* 2008; 26: 77-90.doi: 10.1080/10916460600705790.

Curbelo, F. D. S., Garnica, A.I.C., and Barros Neto, E. L. Salinity Effect in Cloud Point Phenomena by Nonionic Oil Recovery Tests. Petroleum Science and Technology. 2013; 31: 1544 -1552.doi: 10.1080/10916466. 2010. 547906.

Daltin, D. Tensoativos: química, propriedades e aplicações, 5nd ed. São Paulo, Brasil: Blucher; 2011.

Howe, A. M.;Clarke, A.; Mitchell, J.; Staniland, J.; Hawkes, L.; Whalan, C. Visualizing surfactant enhanced oil recovery, Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2015;480: 449-461.doi: 10.1016/ j.colsurfa.2014.08.032.

Israelachvili, J.N. 1992. Intermolecular and Surface Forces, (second ed)Academic Press, London.

Park, S., Lee, E. S., Sulaiman, W. R. W. 2015. Adsorption behaviors of surfactants for chemical flooding in enhanced oil recovery, *Journal of Industrial and Engineering Chemistry*, 21: 1239-1245.doi:10.1016/ j.jiec.2014.05.040.

Santos-Ebinuma, V.C, Lopes, A.M, Converti, A, Júnior, A.P, Rangel-Yagui, C.O. Behavior of Triton X-114 cloud point in the presence of inorganic electrolytes. 2013;360: 435-438.doi: 10.1016/j.fluid.2013.09.053.

Tanford, C. 1980. The Hydrophobic Effect: Formation of Micelles and Biological Membranes. 2nd edition, Wiley, New York.

Thomas, J. E. 2004. Fundamentos de Engenharia de Petróleo, 2nd ed. Rio de Janeiro, Brazil: Interciência.

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