Surfactants Nanocarriers for Enhanced Oil Recovery (EOR)

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ABSTRACT

Chemical methods have been implemented in EOR processes by the addition of surfactants to the injection water. However, most of the surfactant molecules are lost in the reservoir before reaching the oil sites due to their adsorption on the reservoir rock surface, hindering the action of surfactants directly at the water/oil interface and increasing costs. This work proposes the use organic surfactant nanocarriers that would permeate through the reservoir pores and deliver the surfactant at the water/oil interface, decreasing interfacial tension (IFT) and avoiding surfactant losses to the reservoir rock surface. Different types of nanoparticles were produced and evaluated by AFM, SEM, IFT measurements and PCS. The nanoparticles displayed spherical shape and size was in the order of 150 nm. The surfactant nanocarriers were completely soluble in hydrocarbon mixtures, yielding water/oil IFT lower than 1.0 mN/m, which demonstrates the great potential of the surfactant nanocarriers developed to improve enhanced oil recovery methods.

Keywords: surfactant nanocarrier, nanoparticles, enhanced oil recovery, EOR, interfacial tension.

1 INTRODUCTION

A great technological effort has been made to increase the oil recovery from the world's oil reservoirs. Today, the oil recovery by conventional methods (primary and secondary) is sometimes reaching less than 40% of the total oil in the reservoir. The residual oil is trapped in the porous rock structure of the reservoir by capillary forces and cannot be recovered by conventional methods. Thus, enhanced oil recovery methods (EOR) can be applied to increase the oil recovery factor (RF). Chemical methods can be implemented in EOR process in which specifics chemicals are added to the injection fluid and should interact with oil/water/rock system in order to create favorable condition for oil recovery [1].

The most important chemical process of EOR is the surfactant flooding and it is performed by adding surfactants to the water injection. Surfactants have an amphiphilic structure and tend to migrate to w/o interface, reducing the interfacial tension. The changes in interfacial properties tend to decrease the energy of w/o and o/rock interface, improving the displacement efficiency and mobilizing the residual oil into the production well. However, the surfactant molecules are lost in the reservoir due to the adsorption of the surfactants on the surface of the reservoir rock, hindering the action of surfactants directly at oil interface. Surfactant adsorption during the flow of the surfactant solution through the porous media is a factor of major upheavals to chemical EOR process, causing economic losses [2,4].

Nanoparticles for oil recovery from hydrocarbon fields have been studied due to the ability of nanoparticles to modify the surface characteristics of the reservoir. However, the most of the nanoparticles studied have an inorganic nature and tend to migrate integrally to the water/oil/rock interface. Nanopartícles capable to release de surfactant directly into the oil surface has not been reported yet in the literature [3].

Thus, the purpose of this work was the development of surfactant nanocarriers and interfacial tension reducers. The nanocarriers were formed by the blend of surfactants and a non polar solid organic matrix stable in water. The hydrophobic character of the nanoparticles allowed their solubilization in hydrocarbons, increasing the action of the surfactants by their direct release at the oil sites in the reservoir. The developed nanoparticles were called SSN, selective surfactant nanocarriers, due to their capacity to release surfactants directly into the oil/water interface. Results from this study are presented and the potential of the surfactant nanocarriers model for the EOR process is discussed.

2 MATERIALS AND METHODS

2.1 Materials

Blanched beeswax (Sigma-Aldrich, Brazil) was used as solid lipid matrix and the nonionic surfactant was the RENEX100™ (NP10 - (C9H19)C6H4(OCH2CH2)10OH, by Oxiteno). n-Heptan and Toluene (purchased from Vetec Química, Brazil) were used as synthetic oils. Calcium and Sodium Chlorides (Vetec Química, Brazil) were used to obtain the artificial seawater (Brine – 30000 ppm of NaCl and 2000ppm of CaCl).

2.2 Preparation of smart surfactant nanocarriers

The SSN were prepared using hot homogenization methods by ultrasonication. The methodology for obtaining the surfactant nanocarrier was based on the development of nanoparticles for drug deliver. Briefly, the surfactant was dispersed in melted lipid (70°C) to obtain a clean liquid. Then, hot water heated at this same temperature was added to the melted lipid and the phases were stirrer with magnetic bar for three minutes to form the pre-emulsion (o/w). The obtained pre-emulsion was ultrasonified using a probe sonicator UP200S (Hielscher). A power output (amplitude of 80%) was applied for three minutes, leading to the breakdown of the lipid drops by cavitation waves for the formation of the nanoemulsion. The temperature was maintained at 70 °C during the homogenization step by a thermostatic water bath. The nanocarrier was obtained by the cooling down of the nanoemulsion with an ice bath. Nanocarriers were produced with lipid concentration at 1,0 (m/v) and surfactant concentration ranging from 0,1% to 1,0% (m/v) to optimize the procedure.

2.3 SSN Characterization

2.3.1 Particle size measurement

The hydrodynamic diameter and polydispersity index (PDI) were determined by Photon Correlation Spectroscopy (PCS) using a Zetasizer Nano ZS (Marvern Instrument, Germany). The dispersion was diluted with filtrated distillated water at appropriate scattering intensity. The determination was performed at a scattering angle of 175 degrees at 25°C. Each analysis was carried out in triplicate and the data expressed as a mean value. Particle size studies of SSN were carried out at 1h, 24 h and 30 days after preparation.

2.3.2 Scanning electron microscopy – SEM

The morphology of the dried nanoparticles was observed at 20kV using a JSM-6460 (Jeol). Prior to analysis, the nanoparticles suspension was placed on aluminum slides, dried at rum temperature and coated with goad using a sputter coater (K550, Emitech).

2.3.3 Atomic force microscopy – AFM

AFM images were obtained using a Solver Next (NT-MDT). The dispersion was appropriately diluted with distilled water and dropped to a mica surface. After drying in $CaCl_2$ atmosphere, all images were performed in tapping mode using an NSG01 cantilever with resonance frequencies of 115–190 kHz and constant force in the range of 2.5–10 N/m [5].

2.4 Interfacial tension measurements

The interfacial tension was determined by Du Noüy Ring Method. The IFT measurements were used to evaluate the efficiency of the surfactants and nanocarriers in reducing the tension between water and HepTol interface.

The ring method was performed using a digital tensiometer K9 (Krüss, Germany) at 25°C. In this experiment it was used equal volumes (approximately, 25 ml) of the aqueous phase (nanocarriers suspensions at 1% (m/v) of lipid) and organic phase (surfactant solution or Beeswax solution, both at 1% (m/v)). Figure 1 shows the scheme of the experimental apparatus used for the measurements of the interfacial tension. The formulation of water and oil phases studied and the results of interfacial tension are shown at table 2.

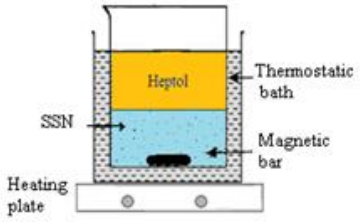

Figure 1 - Schema of the experimental apparatus used to the measurements of interfacial tension.

3 RESULTS AND DISCUSSION

3.1 Characterization of nanocarriers

3.1.1 Effect of surfactant concentration on the particle size

Different surfactant concentrations were used to optimize the procedure to obtain the nanocarriers, as displayed in table 1. The polydispersity index was poorly influenced by the surfactant concentration, differently from the particle size that was reduced from 234 to 118 nm. The increase of NP10 surfactant concentration led to the decrease of the mean particle size caused by the reduction of interfacial tension. The surfactant tends to fill and stabilize the new interface generated through the breakdown of the lipid droplets by the capitation waves [6]. The particle size was optimized with approximately 0.5% of surfactant; however, the surfactant concentration was fixed at 1% for the majority of the incorporations of surfactant in particles.

NP10 concentration (m/v)	1%	0,5%	0,25%	0,1%
Mean size (nm)	118	119	146	234
Polydispersity índex (PDI)	0,26	0,24	0,22	0,29

Table 1: Particle size and PDI as a function of surfactant concentration.

3.1.2 SEM and AFM microscopy

The morphology and the particle size were observed with SEM and AFM images, as shown in Figures 2, 3 and 4, respectively. Both techniques confirmed the spherical particle shape. The AFM image (Figures 2 and 4) show that nanoparticles tend to organize in clusters. This can occur due to the drying process employed in the sample preparation [7]. The diameter of nanoparticles can be estimated through the height profile (Figure 4). This surface relief is compatible with the particles' agglomeration which show particles size with approximately 120 nm in diameter. This result was consistent with the particle size obtained by PCS technique.

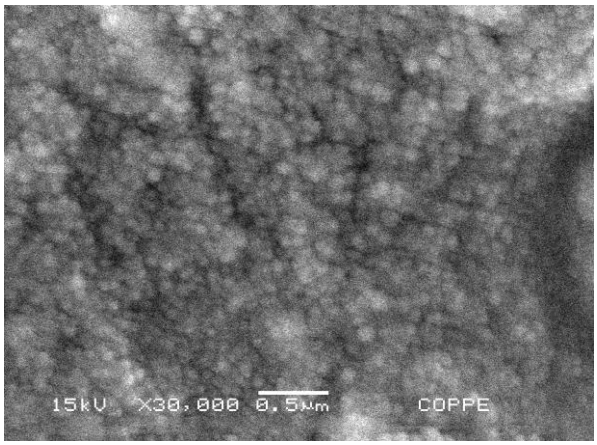

Fig. 2: SEM image of nanocarriers surface, scale bar 0,5µm.

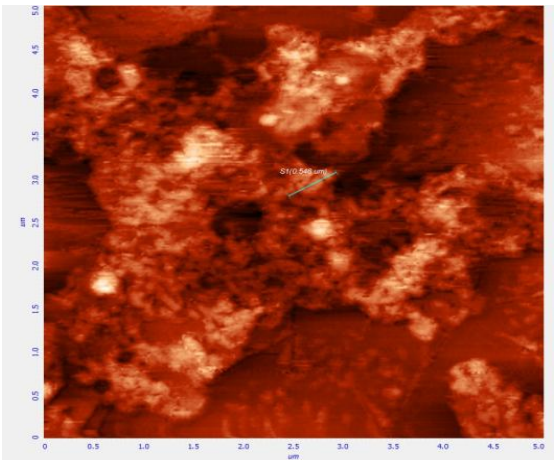

Fig. 3: AFM image of Nanocarriers, scale bar 5 µm.

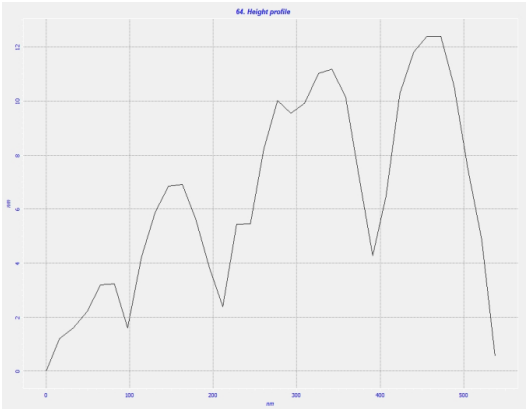

Fig. 4: The corresponding height profile along the dashed line in figure 3.

3.2 IFT measurements by Du Noüy ring

It has been examined the systems containing NP10 solution, mixtures of NP10 and Beeswax (BW), nanoparticles water suspensions and dried SSN. The materials were added to HepTol (50% Heptane, 50% Toluene to simulate the oil) to evaluate their capability to solubilize in oil. Table 2 shows the IFT results for the different formulations, which were analyzed 24 hours after being prepared.

Aqueous Phase	Oil Phase	IFT (mN/m)
Water	HepTol	36,3
NP10 in Water	HepTol	2,0
Water	BW in HepTol	4,0
NP10 in Water	BW mixture in HepTol	< 1 (0,4)
Water	Dried SSN in HepTol	< 1 (0,4)
SSN suspension	HepTol	5,8

Table 2: The formulation of water and oil phases studied and the results of interfacial Tension.

Interfacial tension measurements showed that NP10 and Beeswax have an interfacial activity. The BW is composed by esters and fatty acids that play the role of surfactants, reducing the interfacial tension. It's also important to note that the IFT reduction generated by the NP10 and BW mixture was below the detection limit of the ring tensiometer (< 1,0 mN/m), being lower than the IFT for single components alone. This result suggests that there is a strong synergism between NP10 and BW molecules which could be caused by a better packing of surfactants at the interface. Therefore, the beeswax acts not only as a lipid matrix for the surfactant carriage, but can also work as a co-surfactant, improving the interfacial activity of NP10 surfactant.

The IFT for the dried SSN in HepTol was also < 1,0 mN/m, showing that this Nanocarrier could be solubilized in hydrocarbon and that the resultant interfacial tension of this solution was also below the detection limit of the ring tensiometer, as was the NP10/BW mixture. On the other hand, the aqueous suspension of nanocarriers did not show results that would be compatible with the ones from the solution of NP10/Bw mixture and the dried SSN in HepTol. The high value of IFT obtained for the SSN suspension (5,8 mN/m) suggests that, at the test condition, the nanocarriers in the aqueous suspension couldn`t be solubilized by the HepTol because the interfacial tension values obtained were higher than the values obtained by NP10/BW solution (< 1,0 mN/m).

4 CONCLUSION

The need for new technologies has enabled the development of new methods that would lead to an increase in oil recovery. Thus, we present in this paper a new model of surfactant release that involves nanoparticle systems as surfactant carriers that would promote a more efficient release of surfactants directly in the water/oil interface. In this work, bees wax surfactant nanocarriers were obtained with spherical shape, and 150 nm particle size. The dried surfactant nanocarriers were completely soluble in hydrocarbon mixtures, yielding water/oil interfacial tensions lower than 1.0 mN/m, which demonstrates the great potential of the surfactant nanocarriers developed to improve enhanced oil recovery methods.

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