

## Polystyrene nanoparticles as surfactant carriers for enhanced oil recovery

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**ABSTRACT:** It is well known that oil recovery processes can be increased by surfactant solution injections in the reservoir. However, the high adsorption of this type of compounds on the reservoirs rocks surface is one of the factors that have been preventing the Enhanced Oil Recovery (EOR) development and the economicity of the process. This work presents the synthesis of crosslinked polystyrene nanoparticles (PSNP) and their evaluation as surfactant carriers, able to percolate through the reservoirs pores and to deliver it at the water/oil interface. The nanoparticles were synthesized by emulsion polymerization of styrene and divinylbenzene in the presence of nonylphenol ethoxylate-10 (NF-10EO) or sodium dodecyl sulphate. Photon Correlation Spectroscopy and Interfacial Tension results gave support to the initial supposition that the nanoparticles would swell when in contact with the oil phase, releasing the surfactant at the interface. The nanoparticles obtained with NF-10EO were able to reduce the water/oil interfacial tension to values that were similar to the ones obtained with the aqueous solution of NF-10EO. The results suggest that the PSNP have a great potential to be used as surfactant carriers in EOR. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43789.

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### INTRODUCTION

According to the latest predictions, the global demand for crude oil is being expected to increase during the next years.<sup>1</sup> On the other side, after several years of water flooding in oil recovery processes, the water to oil ratio in the production processes has been increasing, harming the economicity of the oil recovery operations. These results tend to force the premature abandonment of mature fields, leaving as much as 40% of the original oil in place. Enhanced Oil Recovery (EOR) processes aim to decrease the amount of this residual oil that is not recovered by the well natural depletion (primary recovery) or by the reservoir stimulation via immiscible fluids injection, e.g., water and carbon dioxide (secondary recovery).<sup>2–5</sup>

The surfactant solutions flooding employed to reduce the water/oil interfacial tension<sup>6–9</sup> is considered as one of the most promising techniques for an EOR process. When the interfacial tension is reduced, the Capillary Number,<sup>10</sup> which is the ratio between the viscous and the capillary forces, is increased. Thus, the pressure requirement to remove residual oil from a pore is

decreased. However, one of the major issues of this method is the loss of surfactant that occurs by the adsorption of surfactant molecules on the reservoir rock's surface.<sup>11</sup> Therefore, it is an important challenge the development of technologies that would reduce the surfactant losses and still promote the oil displacement.

Nanomaterials have been evaluated to be used in the petroleum industry in some promising applications such as drilling,<sup>12,13</sup> completion,<sup>14,15</sup> and others applications.<sup>16</sup> A great number of research projects are focused on the use of nanotechnology to EOR.<sup>17–24</sup> Polystyrene nanoparticles (PSNP) are gaining interest in different fields.<sup>25,26</sup> The nanometric diameter provides a high surface area to mass ratio, and this property is desirable for delivery applications.<sup>27</sup> Emulsion polymerization reactions are commonly used to prepare PSNP, but the control of the size of the obtained nanoparticles is still poorly understood.<sup>28</sup> Some experimental conditions, such as emulsifier type and concentration, initiator, monomer, stirring conditions and temperature have an influence on the size and on other properties of the particles.

**Table I.** Formulations for Polymerization Reactions and PSNP Particle Sizes ( $D_m$ )

Surfactant	Sample	Surfactant/mM	Crosslinking agent:DVB v/v %	$D_m$ in water/nm	Polydispersity
SDS	01	2.4	0.5	124	0.010
	02	2.4	1.0	105	0.036
	03	2.4	1.5	124	0.003
	04	CMC <sup>a</sup>	1.5	88	0.004
	05	3CMC	1.5	51	0.030
NF-10EO	06	10CMC	0.5	146	0.209
	07	10CMC	1.0	131	0.200
	08	10CMC	1.5	135	0.069
	09	3CMC	1.5	326	0.018
	10	CMC <sup>b</sup>	1.5	402	0.007
	11	10CMC	2.0	123	0,100
	12	10CMC	3.0	151	0,050
	13	10CMC	4.0	176	0,029

<sup>a</sup>CMC(SDS)58.1 mM, bCMC(NF-10EO)50.08 mM; CMC Critical Micellar Concentration.

Preliminary results by our group on the PSNP capacity of oil displacement through flooding tests in unconsolidated porous medium suggested that they have a potential to be used as surfactant nanocarriers for EOR.<sup>29</sup> Nevertheless, this potential could only be established after a more complete study on the effect of different types of surfactants, surfactant concentration and particles suspension purification on the nanoparticles capacity to reduce the oil/water interfacial tension.

This work focuses on the synthesis of PSNP by emulsion polymerization and on the evaluation of the influence of the emulsifier and crosslinking agent concentration on the nanoparticles size, surfactant retention, swelling capacity in the presence of oil, and ability to produce a low interfacial tension between the oil and water phases.

## EXPERIMENTAL

### Materials

Styrene and divinylbenzene (DVB), potassium peroxydisulfate (KPS), sodium dodecylsulfate (SDS), toluene, and n-heptane were purchased from Sigma Aldrich (Rio de Janeiro, Brazil) and nonylphenol ethoxylate-10 (NFE-10) was purchased from Oxiteno (São Paulo, Brazil). All reagents were used as received without any purification. Distilled and deionized water was used throughout the work. Heptol is a mixture of n-heptane and toluene (3:1 v/v) used to simulate oil with a substantial aromatic content. The aqueous salt solution used to simulate brine is a mixture of calcium chloride (1000 ppm), magnesium chloride (1000 ppm), and sodium chloride (3000 ppm).

### Synthesis of Spherical Nanoparticles of Crosslinked Polystyrene (PSNP)

Ten mL of styrene, the specific amount of DVB, and the aqueous surfactant solution were added to a three-necked flask (500 mL) containing 250 mL of deionized water under nitrogen flow and equipped with a condenser sealed with a rubber septum and under magnetic stirring. After 10 minutes the poly-

merization was initiated by the addition of 50 mg of KPS. Then, the temperature was raised to 80 °C and the mixture was stirred for 24 hours.<sup>30,31</sup> The amount of monomer, crosslinker, initiator, and surfactant used are listed in Table I.

### Characterization of PSNP

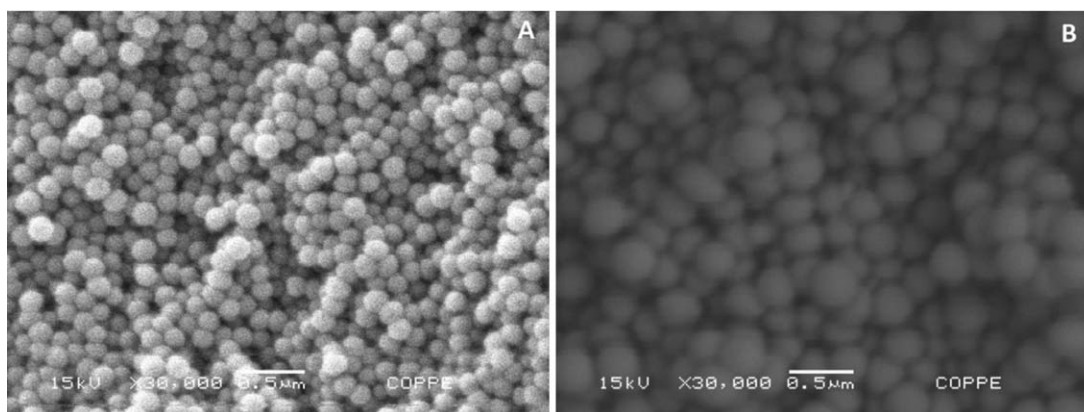
The average particle size ( $D_m$ ) and the polydispersity of PSNP were measured by photon correlation spectroscopy (PCS) (Malvern Zetasizer—MAL 1013334) and the particles morphology was observed by scanning electron microscopy (SEM, JEOL JSM-6460LV) at a voltage acceleration of 15 kV. For SEM analysis and purification methodology, the suspensions containing the nanoparticles were centrifuged with a vacuum centrifuge (Beckman XL-90 Class S), washed several times with deionized water and oven dried half-open for three days at 50 °C.

### Determination of Surfactant Retention by PSNP

To quantify the amount of surfactant that remained in the nanoparticles structure after the synthesis process, two methodologies were used after each cycle of centrifugation. Interfacial tension measurements were performed for the ionic surfactant (SDS) systems until no variation in the interfacial tension results for PSNP-SDS/heptol systems was detected. The nonylphenol ethoxylate-10 (NF-10EO) concentration in the supernatant was quantified, after each cycle of purification, by ultraviolet spectroscopy (UV-Vis) at a wavelength maximum of  $\lambda = 275$  nm. An analytical calibration curve was prepared from 0.05 to 0.8 mM, covering the working concentration range. They were carried out with the necessary number of purification cycles, i.e., until the free surfactant concentration was no longer detectable.

### Evaluation of the Swelling Capacity of PSNP

The crosslinking bonds formed between polystyrene chains by DVB molecules turn these nanoparticles insoluble in any liquids,<sup>32</sup> so in the presence of the oil phase the polymer can only swell. The swelling capacity of the obtained crosslinked nanoparticles was observed by PCS, determining the average



**Figure 1.** SEM: (A) PSNP-SDS-1.5% DVB,  $D_m \approx 120$  nm/(B) PSNP-NF10EO-1.5% DVB,  $D_m \approx 330$  nm.

diameter of the nanoparticles after being re-suspended in water and heptol. For that, the PSNP were re-suspended in heptol or in water with the help of a sonicator (Hielscher, UP2005) for 5 minutes.

#### Interfacial Tension Measurements

The interfacial tension for the systems with PSNP re-suspended in deionized water or in brine with heptol as oil phase was measured until the equilibrium was reached. For comparison, a solution with the same surfactant concentration was employed for the interfacial tension measurements. The interfacial tension was measured by the *Du Nouy* ring method<sup>33</sup> using a tensiometer Krüss (K9ET-Mk1) at 25 °C.

## RESULTS AND DISCUSSION

### Effect of Surfactant Type, Surfactant Concentration and DVB Concentration on Nanoparticle Size

Crosslinked PSNP were synthesized by emulsion polymerization in the presence of two different surfactants, one with ionic character (SDS)<sup>34</sup> and the other with nonionic character (NF-10EO),<sup>35</sup> according to the methodology presented above. The morphology and particle size of the PSNP were characterized by SEM and PCS.

The SEM images showed that the particles have spherical shape and nanometric sizes, regardless of the nature of the surfactant employed, as shown in Figure 1.

The PCS technique showed that the polystyrene particles exhibit a narrow particle size distribution as shown in Table I.

In emulsion polymerizations, the surfactants are commonly used above the critical micelle concentration (CMC), the minimum surfactant concentration at which the micelles are formed, but when it is not expected micelles into the solution, the polymerization occurs by the surfactant migration into the solution stabilizing drops of monomer and minimizing free energy of the system. As the amount of surfactant is small, the drops will be larger.<sup>36</sup> Another observation was that increasing the surfactant concentration tends to decrease the PSNP size (Table I). This would be expected because the increase of surfactant concentration would thermodynamically favor the formation of a larger number of smaller micelles, stabilizing smaller monomer drops, where polymerization occurs.<sup>37</sup>

A comparison of the size of nanoparticles synthesized with SDS (sample 4) and the ones synthesized with NF-10EO (sample 10), at the same reaction conditions (surfactant at CMC concentration and 1.5% DVB), shows that the average diameter of the sample 10 particles is much larger than that of sample 4 nanoparticles. Ionic surfactants have a larger capacity to reduce the size of the nanoparticles than nonionic surfactants, because they exhibit different emulsion stabilization mechanisms during the polymerization. In the case of anionic surfactants, such as SDS, the ionic surfactant forms a charged layer at the interface which is neutralized by water counter ions, forming a double layer. The dispersed phase droplets act as charged particles and the emulsion is stabilized by repulsive electrostatic forces. The nonionic surfactants can adsorb on the surface of the dispersed phase droplets providing a volume restriction (steric stabilization) that protects the particles from contact and coalescence.<sup>38,39</sup> The ionic repulsion forces are more effective than the steric ones and, therefore, the nonionic surfactants tend to give larger nanoparticle sizes, corroborating the results shown in Table I. The reduction in the interfacial tension is a consequence of the efficiency of the surfactant employed and of the amount of surfactant available to be released at the interface. The larger number of smaller nanoparticles produced by SDS leads to larger amounts of surfactant retained at the total surface and later delivered at the water/heptol interface, leading to lower interfacial tensions.

For both surfactants studied and for the samples synthesized with the same amount of surfactant, the results show the same tendency of nanoparticle size oscillation with increasing of crosslink agent, as previously reported by Jiang Kai.<sup>32</sup> The expected trend would be of a decrease of particle size with the increase of DVB content, as shown by some of the samples obtained in our work. However, some samples (03 and 08) did show a particle size slightly larger than expected and this might be because of a tendency for agglomeration of the smaller nanoparticles.

#### Purification Process

**Effect of the PSNP Suspensions Purification Process on Particle Size.** The nanoparticles suspensions were purified through several cycles, until the presence of free surfactant was not detected. After purification, the PSNP were re-suspended in

**Table II.** Interfacial Tension Results for Water/Heptol Systems Using PSNP-SDS 1

Sample	Purification	$\gamma$ (mN/m)
Water (Reference)	—	40.1
SDS (8.7 mM > CMC)	—	4.5
SDS (2.4 mM)	—	9.7
O1	PSNP_dry <sup>a</sup>	9.8
O1	PSNP_1 °centr. <sup>b</sup>	10.6
O1	PSNP_2 °centr. <sup>b</sup>	11.7
O1	PSNP_3 °centr. <sup>b</sup>	11.9

<sup>a</sup>[SDS] = 2.4 mM.

<sup>b</sup>[SDS] < 2.4 mM.

water and their average diameter was found to be the same as the ones before purification, as shown in Table I. These results show that no agglomeration did occur during the purification and the re-suspension processes.

#### Effect of PSNP Suspensions Purification Process on the Solutions Surfactant Concentration and Surfactant Retention Analysis.

**PSNP-SDS.** For the obtained suspension of PSNP-SDS the surfactant in solution was not directly quantified by UV during the purification process, since it does not absorb in this region of the spectrum. Instead, an indirect analysis was performed by interfacial tension measurements. It was observed that when the particles suspensions were purified the interfacial tension increased because of the loss of surfactant that remained in solution after completion of the synthesis. After the third purification cycle no variation in the interfacial tension was detected for all the PSNP-SDS. In the subsequent experiments only purified PSNP suspensions were used to measure just the effect of the surfactant trapped in the nanoparticles. The interfacial tension results from each purification cycle for the nanoparticle re-suspended in water and heptol systems using the PSNP-SDS 1 (SDS 2.4 mM and DVB 0.5%) are shown in Table II.

In all the systems presented in Table II it was used the same concentration of the PSNP (0.25% m/v) re-suspended in deionized water.

**PSNP-NF-10EO.** Because of the fact that it would be easier to quantify the surfactant concentration in the aqueous medium for a larger number of samples if UV-Vis could be employed, NF-10EO was also used to obtain the PSNP. Therefore, UV-Vis measurements were carried out to quantify the nonionic surfactant (NF-10EO) concentration that remained in solution after the purification cycles for PSNP-NF-10EO. The concentration of NF-10EO retained in the nanoparticle structure (Table III) was determined by the difference between the concentration of surfactant employed in the synthesis and one of the free surfactant, which was eliminated in the purification. The surfactant percentage retained was calculated by the ratio between the mass of surfactant retained in the nanoparticle and the mass of surfactant introduced in the reaction medium.

Table III shows that increasing DVB concentration tends to increase the surfactant percentage that remains in the PSNP. This result can be interpreted as because of an increase of the degree of crosslinking, i.e., to an increase of the number of small cavities in the polymeric structure. Inside these smaller cavities, the surfactant molecules remain even more trapped, and it causes a lower surfactant loss during the purification process. Then, when the PSNP is re-suspended in heptol, occurs the nanoparticle swelling and the release of a greater amount of surfactant.

#### Nanoparticles Swelling Capacity in the Oil Phase and interfacial Tension Results

Table IV shows the particle size, swelling percentage, and interfacial tension results for PSNP samples re-suspended in water/heptol systems. As expected, the particles average diameter increased when the PSNP were re-suspended in heptol (Table IV). This measurement shows the swelling capacity of PSNP in oil, an important result to support the proposed mechanism for the release of surfactant in the application of the PSNP in chemical EOR methods, avoiding loss of surfactant by adsorption on rock. The process of oil uptake by the PSNP is essential for the release of the surfactant to occur in the water/oil interface, but the amount of the oil will depend on PSNP size and degree of crosslinking. Therefore, it is important to control the nanoparticles size to avoid their retention in the porous medium during the EOR injections.

It should be noticed that most of the PSNP diameters after swelling are still smaller than the average diameter of the pores of the reservoir rocks, which, as previously mentioned, is about 0.1–0.5  $\mu\text{m}$ .<sup>40</sup> As a result, the PSNP should not clog the pores of the reservoir. In addition, a considerable reduction of the interfacial tension, as compared with the reference system, was observed for all PSNP, showing an efficient release of surfactant by the nanoparticles.

Figure 2 helps to show that although the particle size tends to decrease with the increase of crosslinking agent concentration, it appears to be levelling off at a certain DVB concentration, suggesting that perhaps, at this point, a maximum crosslinking degree has been reached. Also, the figure corroborates with the suggestion that the oscillation in particle size could be because of an agglomeration of nanoparticles, since it is happening at the smaller particle size range.

**Table III.** Surfactant Retention in PSNP-NF-10EO Samples

Surfactant	Sample	NF-10EO Retention %
NF-10EO	O6	48,0
	O7	49,1
	O8	50,6
	O11	53
	O12	70
	O13	76,5



**Table IV.** Particle Size, Swelling Percentage, and interfacial Tension Results for PSNP Samples Re-Suspended in Water and Heptol

Surfactant	Sample	$D_m$ in heptol/nm	Polydispersity	Swelling %	$a_\gamma$ (mN m <sup>-1</sup> )
SDS	01	227	0.194	90	11.9
	02	200	0.003	84	9.9
	03	196	0.156	59	8.2
	04	145	0.644	65	7.9
	05	90	0.762	76	7.4
NF-10EO	06	375	0.860	157	6.2
	07	310	0.670	136	5.4
	08	295	0.670	120	4.0
	09	800	0,741	145	8.7
	10	798	0,705	99	10.7
	11	244	0,594	98	4.0
	12	202	0,740	68	4.0
	13	267	0,572	56	4.0

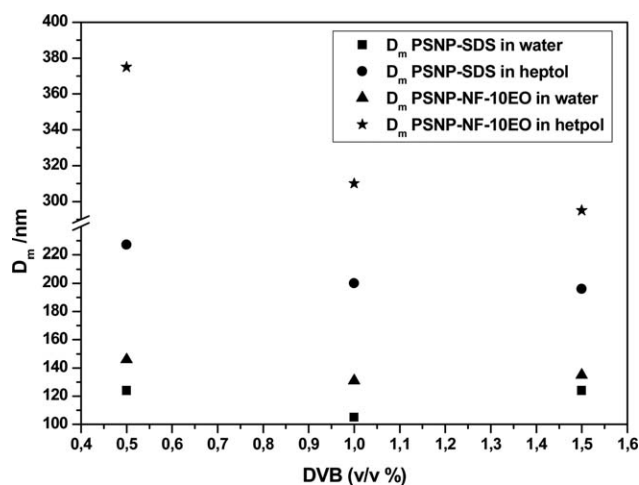
<sup>a</sup> Standard comparison: SDS > CMC (4.5 mN m<sup>-1</sup>), NFE-10EO > CMC (3.9 mN m<sup>-1</sup>) and reference: water (40.1 mN m<sup>-1</sup>).

### Effect of DVB and Surfactant Concentrations on the interfacial Tension and Swelling Capacity of Nanoparticles in Oil Phase

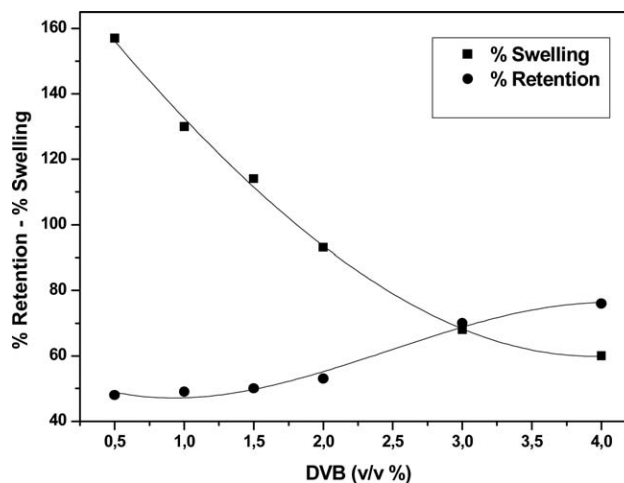
**PSNP-SDS.** The influence of the crosslinking agent concentration on the amount of surfactant released was evaluated by interfacial tension measurements. The results in Table IV show a larger reduction in the interfacial tension for a higher degree of PSNP crosslinking (samples 1–3), indicating that larger amounts of surfactant are retained in the nanoparticle as the degree of crosslinking increases. The swelling behavior observed from the results in Table IV can also be related to the degree of crosslinking as the swelling decreases with the increase of crosslinking agent concentration (samples 1–3). This behavior is because of the fact that higher degrees of crosslinking in a polymer make its swelling more difficult as the materials structure becomes more rigid. Besides, a higher number of crosslinking bonds should favor the retention of a larger number of surfactant molecules per particle.

**PSNP-NF-10EO.** Several experiments were performed to investigate the influence of the degree of crosslinking and of the amount of surfactant used on the PSNP properties. These results were shown in Tables III and IV, and for comparison purpose, the swelling behavior and surfactant retention results are plotted in Figure 3.

The results for the PSNP-NF-10EO swelling capacity, the water/heptol interfacial tension and the surfactant retention capacity exhibit the same tendency as the ones obtained for the PSNP-SDS systems. The results show that increasing the DVB concentration decreases the nanoparticles tendency to swell, the water/heptol interfacial tension, and increases the nanoparticles capacity to retain surfactant molecules (samples 6–8, 11–13). Also, increasing the surfactant concentration in the polymerization process reduces the interfacial tension of the systems, although it is not possible to say that there is a correlation between the surfactant concentration and the swelling capacity



**Figure 2.** Effect of DVB concentration (v/v %) on particle size of PSNP at constant surfactant concentration: SDS (2.4 mM), NF-10EO (0.8 mM).



**Figure 3.** Effect of crosslinking agent concentration of the PSNP-NF-10EO on their swelling capacity in heptol and on their surfactant retention capacity.

**Table V.** Interfacial Tension Results for Aqueous Phase/Heptol Systems

System	$\gamma$ (mN m <sup>-1</sup> )
Water	40.1
Brine	38.3
NF-10EO $\geq$ CMC-Water	3.9
NF-10EO $\geq$ CMC-Brine	3.0
10	10.7
09	8.7
08	4.0
10-Brine	9.8
09-Brine	7.3
08-Brine	3.0

of the nanoparticles (samples 8–10). The results also suggest that the ionic character of the surfactant has no influence on the PSNP properties other than the nanoparticle size. In addition, increasing the surfactant concentration in the medium helps the stabilization of even smaller styrene droplets in the emulsion formed during the polymerization process. Consequently, a larger amount of surfactant can be retained as the total surface available increases with the number of smaller nanoparticles, thus leading to a higher amount of surfactant to be later released at the water/heptol interface and to a larger reduction of the interfacial tension of the system (samples 8–10).

#### Influence of Brine on the Interfacial Tension

**PSNP-NF-10EO.** Table V shows the interfacial tension results for samples 8–10, and also for a standard solution containing the equivalent concentration of surfactant retained by PSNP and for blank samples in both systems: heptol/water and heptol/brine. The brine formulation used is described in Materials section.

As previously observed, increasing the surfactant concentration in the nanoparticles resulted in lower water/oil interfacial tension values. The interfacial tension reduction observed for the sample 8 was equivalent to the one observed for the standard for both systems. The results also show lower values when in the presence of salt.

The increase of salt concentration in the medium has an effect on the size of the surfactants polar group, reducing its size and allowing a better packing at the interface. The increase of the ionic force of the water medium will also favor a migration of the surfactant molecules to the interface, and these two effects will lead to a higher reduction of the interfacial tension.

This result is very interesting for EOR applications because it means that sea water or production water could be used to resuspend the nanoparticles before the injection.

#### Proposed Model for the Behavior of PSNP in EOR Projects

The results of this study have shown that, regardless of the nature of the surfactant, it is possible to obtain crosslinked PSNP which are able to swell when in contact with oil, releasing the surfactant employed in its preparation and reducing the oil/

water interfacial tension. The proposed mechanism of action of PSNP in oil is shown in Figure 4.

#### CONCLUSIONS

The results have shown that in an aqueous medium, a large percentage of the mass of surfactant employed in the PSNP preparation remains trapped in the nanoparticles microstructure. However, when in contact with the oil phase, swelling of the nanoparticle occurs, and this is followed by the release of surfactant into the medium, reducing the water/oil interfacial tension.

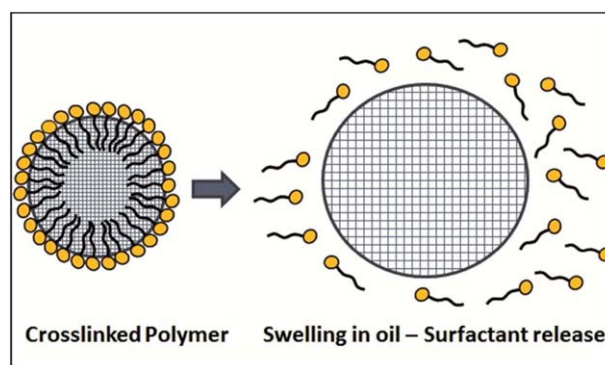
The degree of crosslinking (%DVB) of the nanoparticles has an influence on their performance in the water/oil system. The results show that the higher the degree of crosslinking, the greater will be the reduction in the interfacial tension when in contact with oil and also lower will be the nanoparticles swelling.

Moreover, increasing the surfactant concentration in the synthesis of the nanoparticles reduces the particle size. This also conducts to lower water/oil interfacial tension when incremented with the best degree of crosslinked agent.

The nanoparticles obtained with NF-10EO (NF-10EO-PSNP) were able to reduce the water/oil interfacial tension to similar values to the ones obtained with the standard sample, the aqueous solution of NF-10EO.

The PSNP-NF-10EO samples were more efficient in the release of surfactant when in the presence of salt solutions. This result is quite interesting because the test took into account an important reservoir condition that is the presence of brine.

Finally, the model proposed for the controlled release of surfactant, in the water/oil interface, from PSNP is a promising system for improved methods of chemical EOR, since it would avoid surfactant losses through adsorption on the reservoir rock surface. These particles present the advantage of reducing the mass of surfactant injected for the chemical EOR process by releasing the surface active agent only at the water/oil interface.



**Figure 4.** Schematic model for the mechanism of surfactant release of PSNP when in contact with the oil. [Color figure can be viewed in the online issue, which is available at [www.wileyonlinelibrary.com](http://www.wileyonlinelibrary.com).]

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