Polymer Nanofluid for Enhanced Oil Recovery: A Design of polystyrene nanoparticles, Transport Behavior Evaluation and Unconsolidated Flooding Test

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ABSTRACT

Nanomaterials can contribute to the petroleum industry with some promising applications, such as nanofluids for enhanced oil recovery (EOR) and drilling. This work provides a new surfactant containing nanoparticles which is able to percolate the porous media and deliver the surfactants at the water/oil interface, minimizing the loss of surfactant in the process. Cross-linked polystyrene nanoparticles (NPPS) were synthesized by emulsion polymerization and characterized. Column tests were also made to study the NPPS transport in the porous media and the oil recovery in an unconsolidated sandpack. The results show that the particles have spherical shape and nanometric size, smaller than the common pore dimensions. Another observation from the PCS analysis was that the nanoparticles mantained their original size when re-suspended in water showing that aggregation did not occur. The surfactant retention was around 60%. The recovery factor for the nanofluid was larger than the one obtained for the surfactant alone.

Keywords: nanofluid, EOR, oil, polystyrene, nanoparticles.

1 INTRODUCTION

The application of nanotechnology in the Oil & Gas industry has been widely reported in both upstream and downstream applications. An example of these are the nanofluids (smart fluids) which consist on stable suspensions of particles with nanometric dimensions. The incorporation of nanoagents in the system offers several advantages, such as the use of nanoparticles for enhanced oil recovery. The particles could act as surfactant carriers and minimize its loss by adsorption on the reservoir rock, which is a major economic disadvantage of the use of chemicals in enhanced oil recovery. Recent publications showed positive results in enhanced oil recovery applications [1] [2], [3]. This work focuses on the design of a polymer nanoparticle containing surfactants to be used in an aqueous suspension as a nanofluid for enhanced oil recovery. The nanoparticles are formed by crosslinking chemical reactions [4]; thus, they have the are insoluble in water and can only swell in the presence of oil. Therefore, when in contact with oil, the nanoparticle swells, releasing the surfactant into the medium and reducing the interfacial tension of the water/oil systems. Figure 1 shows a scheme of this mecanism.

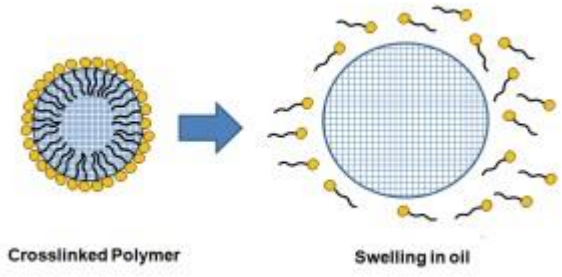

Figure 1- Schematic illustration of NPPS swelling process.

2 EXPERIMENTAL

2.1 Materials

Styrene, divinylbenzene (DVB) (55%), n-decane (99%), potasium peroxidissulfate (KPS)(99%) and toluene (99.5%)were purchased from Sigma AldrichCompany (Rio de Janeiro, Brazil), and nonylphenol ethoxylate -10 (NFE-10EO) (99%) was purchased from Oxiteno (São Paulo, Brazil). All the reagents were used as received without any purification. Distilled and deionized water was used throughout the work.

2.2 Synthesis and Purification of spherical nanoparticles of crosslinked polystyrene NPPs

Styrene, DVB and surfactant were added in a three-necked flask (500 ml) containing 250 ml of deionized water under nitrogen flow and magnetic stirring. After 10 minutes the polymerization was initiated by the addition of 50 mg of KPS. Then, the temperature was raised to 80 °C and the mixture was stirred under nitrogen flow for 24 hours. The amounts of monomer, crosslinker, initiator and surfactant used are listed in Table 1.

Table 1- Reagents amounts used in polymerisation.

Sample	Styrene (ml)	DVB (%)	NF10EO (mM)
1	10	1,5	0,08*
2	10	1,5	0,24**
3	10	1,5	0,8***
4	10	1,0	0,8***
5	10	1,5	0,8***
6	10	2,0	0,8***
7	10	3,0	0,8***
8	10	4,0	0,8***

* CMC, ** 3CMC, *** 10CMC

After 24 hours, the suspensions containing the nanoparticles were separated in a vacuum centrifuge (Beckman XL-90 Class S), rotor 70Ti, rotor speed of 45000 RPM, at 10°C for three hours. The nanoparticles were washed with deionized water and were centrifuged three times. Then, were dried on a half-closed door oven at 50 °C for three days. The NPPs were resuspended in media mentioned above with the aid of a sonicator (Hielscher, UP2005) for 5 minutes.

2.3 Characterization of NPPs

The NPPS morphology was characterized by Photon Correlation Spectroscopy (PCS) using a Zetasizer (Malvern Nano ZS), and scanning electron microscopy (SEM) (JEOL JSM – 6460 LV (15 kV)). The surfactant retention in the nanoparticles was determined by ultraviolet spectroscopy (UV) (BiospectroSP-220). The swelling capacity of the cross-linked nanoparticles was observed by PCS, and the interfacial tension was measured by the Du Nouy ring method using a Krüss K9ET-MK1tensiometer.

2.4 Nanoparticle Mobility in Porous Media

The transport of the nanoparticles was investigated for potential EOR applications in an unconsolidated sandpack (shivered between 30 and 270 mesh). The procedure used consisted of the following steps: First, the sandpack is preflushed with 2 pore volumes (PV) of distilled water. Then, 5PV of NPPs solution are injected into the sandpack followed by 5PV of distilled water while collecting samples of the effluent. The fractions collected were quantified by a linear behavior of the NPPs solution turbidity measured on the spectrophotometer. A summary of experimental conditions is shown in Table 2. The column test set-up is presented in Figure 2.

Table 2- Conditions of column test.

Conditions	
Porosity	0,35
Pore Volume	7,0 ml
Q (ml/min)	0,5ml/min

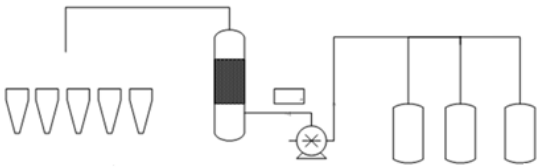

Figure 2- Schematic illustration of column test set-up.

2.5 Oil Displacement in Porous Media

The improvement of oil recovery by using the nanofluid and surfactant alone was investigated for potential EOR applications. A mixture of decane / toluene (3:1vol/vol) was chosen to represent the oil phase.

The injection procedure used:

1 - 2 PV water injection
2 - 2 PV oil injection (S_{oi})
3 – X * PV water injection (S_{or} after water injection).
4 - 3 PV surfactant or nanoparticle injection.
5 – Y * PV water injection (S_{or} after tertiary recovery).

* X and Y values are the required number of PV of water until no more oil is produced. These values are characteristic of each test.

3 RESULTS AND DISCUSSION

3.1 Morfology of NPPs

Crosslinked polystyrene nanoparticles (NPPS) were synthesized by emulsion polymerization in the presence of a non-ionic surfactant (NFE-10EO) following the methodology described above. The NPPS were characterized by SEM and PCS techniques.
PCS technique verifies that the polystyrene particles exhibit nanometric size with a narrow distribution. Moreover, the percentage of crosslinking agent does not influence the average particle diameter considerably as does the concentration of the surfactant (Table 3).

Table 3 - Average diameter (Dm) and polidispersity of NPPs in aqueous suspension.

Sample	Dm (nm)	Polidispersity
1	401,8	0,007
2	326,4	0,018
3	146,0	0,209
4	131,3	0,200
5	134,6	0,069
6	122,8	0,100
7	150,8	0,050
8	176,3	0,029

The SEM images (Figure 3-4) confirm that the particles have spherical shape and nanometric size.

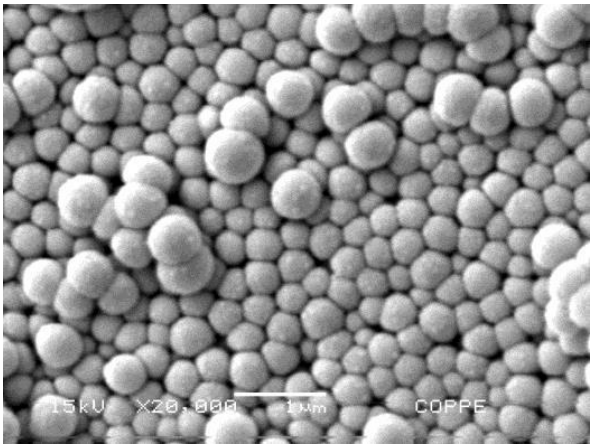

Figure 3- Sample 1- SEM image magnification = 20000X.

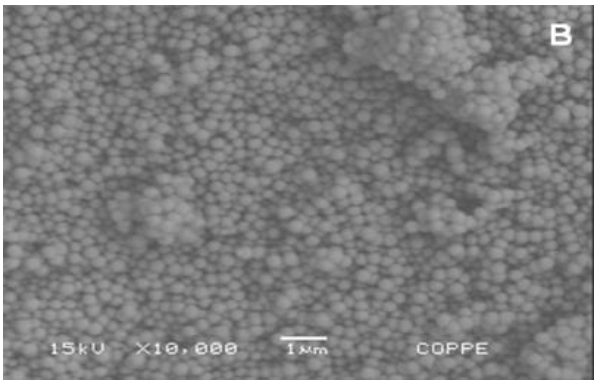

Figure 4- Sample 8- SEM image magnification = 10000X.

3.2 Surfactant Retention and Swelling Capacity

The remnant surfactant concentration after the purification process of the NPPs was quantified by UV-Vis. The amount of surfactant retained was calculated by a mass balance. All the samples have a retention greater than 50%. The PCS technique showed the average diameter of the NPPs increased when they are re-suspended in oil. Which agreeing This is in agreement with the proposed mechanism described in the introduction of this article. A graphic of the concentration of surfactant retained as a function of the swelling percentage according to the degree of crosslinking of the polymer chain in the NPP was plotted (Figure 5). The trend of the curve shows that for concentrations of DVB greater than 3.0%, there is a minimum value for the tendency to swell. In other words, regardless the degree of crosslinking of the polymer, there is no significant difference in average particle size in oil above 3.0% DVB.

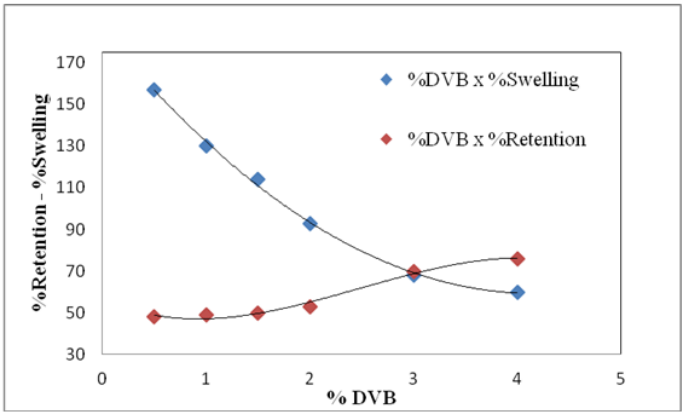

Figure 5- Retention of surfactant as a function of the swelling percentage according to the amount of DVB in NPPs.

3.3 Interfacial Tension Measurements

A ring tensiometer was used to determine the interfacial tension between water and the oil phase. The different water phases used were: distilled water, brine, NPPs suspension and surfactant solution (NFE-10EO) The brine was composed of $CaCl_2$ (1000 ppm), $MgCl_2$ (1000 ppm) and NaCl (30000 ppm). Table 4 is a comparison of the different systems and the interfacial tension observed.

Table 4- Interfacial tension measurements.

System	γ(mN/m)	System	γ(mN/m)
Water	40,1	Sample 5	3,0
Brine	38,0	Sample 6	2,5
NFE-10EO*	3,0	Sample 7	2,4
Sample 3	2,5	Sample 8	2,3
Sample 4	3,0		

* surfactant solution with concentration equal to 10CMC.

Similar values of interfacial tension were observed for the surfactant solution and the NPPs solutions, showing that the nanofluid has an equivalent capacity to reduce interfacial tension between water and oil. In addition, the use of NPPs has the advantage of releasing the surfactant only in the presence of oil, preventing the adsorption on the rock.

3.4 Nanoparticle Mobility in Porous Media

Figure 6 shows an example of NPPs concentration in the effluent as a function of PV injected. The blue dots are the nanoparticles concentrations in the effluent measured by turbity (at a wavelength of 400nm). The fraction of nanparticles recovered was calculated by perfoming a mass balance in the pore volumes injected and the volume eluted. The total NPPs recovery it was 51%.

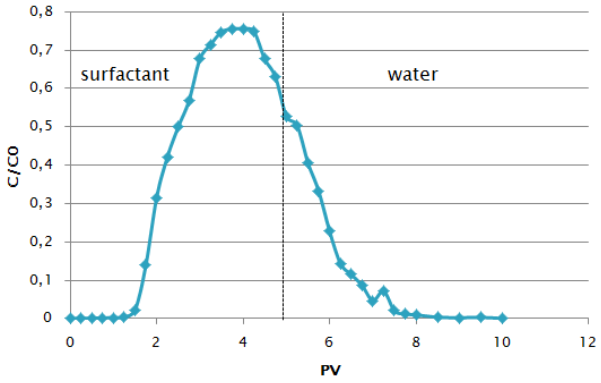

Figure 6- Effluent concentration history of sample 7.

3.5 Oil Displacement in Porous Media

Effluent samples were collected every 7,0 ml (PV volume) in 10ml graduated tubes. The tubes were capped and the levels were read immediately. Oil recovery tests were performed for three systems using Sample 7: NPPs solution before the purification step, purified NPPs solution and surfactant alone solution in the same concentration than the one used for the polymerization reaction (0,08mM). The purpose of this test was to evaluated the potencial of these systems in oil recovery. The results are presented in table 5.

Table 5- Oil recovery data using: (a) NPPs solution before the purification step; (b) purified NPPs solution, and (c) surfactant alone (0,08mM).

(a)	
Sor	65,71%
Frf	15,22%
(b)	
Sor	62,86%
Frf	11,36%
(c)	
Sor	57,14%
Frf	15%

The three systems were successful in flowing through the sandpack. However, the sandpack is unconsolidated causing differences in the values of residual oil saturation. To normalize this difference the final recovery factor (Frf) was calculated. The Frf is the ratio of oil recovered after chemical product injection and oil recovered after water injection. It should be noticed that although the recovery factor obtained for the purified NPPS suspension is 3,63% lower than the one obtained with the surfactant solution, the concentration used in the former is half the one in the latter.

4 CONCLUSIONS

The results suggest that in the aqueous medium a reasonable fraction of the surfactant remains trapped in the nanoparticles. However, when in contact with the oil swelling occurs,, followed by the release of surfactant into the medium, reducing the interfacial tensionbetween the water and the oil.

Increasing the concentration of the surfactant used to obtain the nanoparticles reduces the particle size and the interfacial tension between the water and the oil. The degree of cross-linking (DVB content) of the nanoparticles has a minor influence on interfacial tension reduction.

The recovery factor obtained with the NPPS suspension is similar to the one for the pure surfactant proving that these systems have potential for enhanced oil recovery applications. The success of the NPPs serves as a model evidencing that it is possible to use other surfactants to get a more efficient reduction of the interfacial tension.

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