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Preliminary evaluation of amphiphilic block polyelectrolytes as potential flooding agents for low salinity chemical enhanced oil recovery

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ABSTRACT

Amphiphilic block polyelectrolytes are known for their remarkable thickening properties in water solution, originating from their ability to self-assemble into large micellar aggregates. This makes them promising flooding agent for chemical enhanced oil recovery (cEOR). However, to the best of our knowledge, they have not yet been directly investigated for this purpose. In this work, a survey of relevant properties for EOR (rheology, filterability and emulsification), and laboratory scale oil recovery experiments, were performed on water solutions of polystyrene-block-poly(methacrylic acid) amphiphilic block polyelectrolytes, and compared with a commercial partially hydrolyzed polyacrylamide (HPAM), to evaluate the real potential in EOR applications for the first time. It was found that the recovery of amphiphilic block copolymers in low salinity brine (0.2% concentration of NaCl) is remarkably higher than that of HPAM at comparable weight concentration and shear viscosity, despite a much lower molecular weight. Effect of salinity and emulsification properties of the studied polymers have also been preliminarily investigated. Our results suggest that the recovery mechanism of these polymers differs from the traditional mechanism of polymer flooding, possibly due to emulsification of the oil. In conclusion, the studied amphiphilic block polyelectrolytes show promise as chemical agents in low salinity polymer flooding.

1. Introduction

Despite the ongoing paradigm shift towards green and sustainable sources of energy and materials, humanity will still be dependent on fossil fuels for decades (Abas et al., 2015; Mohr et al., 2015; Raffa and Druetta, 2019). Traditional chemical enhanced oil recovery (cEOR) techniques still suffer several limitations (Saboorian-Jooybari et al., 2016; Sheng et al., 2015), which includes high degradation rate, loss of chemicals and plugging by adsorption on rocks and precipitation, etc., therefore research of new substances and methods, (e.g., nanoparticles flooding), is still very active (Druetta et al., 2018, 2019; Sheng, 2017; Sheng et al., 2015; Wever et al., 2011). Traditional cEOR includes several techniques, of which polymer flooding is the most mature one (Druetta et al., 2019; Raffa and Druetta, 2019; Saboorian-Jooybari et al., 2016; Sheng et al., 2015; Wever et al., 2011).

The main recovery mechanism in polymer flooding is based on mobility control, which is optimal when the mobility ratio (M) approaches unity. M is a dimensionless number, dependent on the viscosity of oil and displacing fluid, as well as their relative rock permeability, as expressed in Equation (1) (Maia et al., 2009; Wever et al., 2013), where

λ stands for mobility, k for permeability and η for viscosity (indexes o and w are for oil and water phase, respectively). The role of mobility control in oil recovery is discussed in many reviews and books (Druetta et al., 2019; Lake, 1989; Raffa and Druetta, 2019; Sheng, 2010; Wever et al., 2013). In short, polymer flooding allows to reduce mobility of the water phase by increasing its viscosity, improving the sweep efficiency of the process, and therefore the oil recovery.

$$M = \frac{\lambda_w}{\lambda_o} = \frac{k_w/\eta_w}{k_o/\eta_o} = \frac{k_w \eta_o}{k_o \eta_w} \quad (1)$$

There are in fact different mobility ratios (end point M , shock front M and total M), which have in principle different values (Beliveau, 2009); the one generally considered is the end point mobility ratio, although it is reported that recovery can still be good if this value is high, (Zhang and Seright, 2014). End point M can be calculated in polymer flooding (Koh et al., 2018).

In practice, it is difficult to estimate any M in a polymer flooding process. One reason is that estimating the actual value of viscosity for the water phase is not trivial. As polymer solutions are strongly non-Newtonian, the values will depend on the experienced shear (or

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elongational) stress, which will vary based on flow characteristics, temperature, rock porosity and other reservoir and well parameters. It is possible to include non-Newtonian behavior in the calculation of end point M using fractional-flow theory (Koh et al., 2018). However, an accurate estimate of mobility ratios would require the determination of permeability changes during flooding, therefore, for simplicity, in this work we will just consider the viscosity ratio, and we will compare different polymers based on this value.

Polymer flooding is traditionally performed with partially hydrolyzed polyacrylamides (HPAM) or, to a much lower extent, biopolymers. Various polymers have been proposed and studied as alternatives to HPAM, to overcome known problems connected with polymer hydrolysis, degradation and adsorption. This has been the subject of several reviews in recent times (Kamal et al., 2015; Raffa et al., 2016a; Raffa and Druetta, 2019; Sheng et al., 2015; Standnes and Skjevrak, 2014; Wei, 2016; Wever et al., 2011). Among the studied classes of polymers, particularly interesting are hydrophobically associating ones. These are usually polyacrylamide derivatives, incorporating low amounts of hydrophobic monomers (Yu et al., 2019; Zhang et al., 2008). It is well established that the presence of hydrophobic domains affects rheological properties via intermolecular associations (Afolabi et al., 2019; Bai et al., 2018; El-hoshoudy et al., 2017; Wever et al., 2011; Zhong et al., 2018). Surprisingly, although it is known that often hydrophobically modified polymers also possess interesting interfacial properties (Raffa et al., 2016b; Su et al., 2019), these have not been generally taken into account when discussing such systems (Raffa et al., 2015, 2016a) until recently (Liu et al., 2019). Indeed, hydrophobically modified water-soluble polymer can be classified as polymeric surfactants, which have been suggested as possible substitutes for surfactant-polymer flooding (Raffa et al., 2016a). They can improve oil recovery by mobility control as traditional polymers, but also by other mechanisms associated with surfactant flooding, such as capillary desaturation, wettability alteration, and emulsification of the oil, possibly avoiding some of the problems associated with surfactant-polymers mixtures (Co et al., 2015; Raffa et al., 2016a; Raffa and Druetta, 2019; Sheng, 2010).

We have shown in previous research that polystyrene-block-poly(methacrylic acid) amphiphilic block copolymers (PS-*b*-PMAA) possess remarkable thickening properties in their salt form in water solution (Meijerink et al., 2017; Raffa et al., 2013, 2014), making them suitable systems for cEOR, due to the possibility to achieve a favorable viscosity ratio. Compared to commercial polymers used for cEOR such as HPAM, they possess much lower molecular weight, which could be beneficial in reducing adsorption on the rocks and pores plugging phenomena, as well as shear degradation. Also thermal stability is potentially improved,

as these polymers do not contain hydrolysable groups, and thermal degradation should not be significant in ordinary reservoir conditions, based on TGA data of copolymers of styrene and methacrylate, which do not decompose below 200 °C (Migliore et al., 2020). Moreover, their amphiphilic nature could have the beneficial effects previously mentioned for polymeric surfactants, namely the possibility to increase both macroscopic and microscopic displacement (Kamal et al., 2017; Raffa et al., 2016a).

Despite the potential of amphiphilic block copolymers as flooding agents for enhanced oil recovery, to our knowledge they have not been directly investigated for such application. Although from a chemical point of view, they can be classified as hydrophobically associative polymers, these systems are known to form rather different aggregates in water solution, resulting in different properties (Raffa et al., 2016a). In particular, the improved thickening abilities come from different mechanisms: while associative polymers commonly tested for EOR are characterized by long hydrophilic chains with short hydrophobic “stickers”, able to improve rheological properties via formation of transient networks in solution, the systems proposed here form stable large micellar aggregates, with increased hydrodynamic volume, and therefore higher viscosity at a comparably much lower molecular weight (Fig. 1). It is important to notice that these aggregates are usually non-dynamic (so-called “frozen”), meaning that the association in this case is not concentration dependent (Nicolai et al., 2010; Raffa et al., 2015). In this respect, amphiphilic block polyelectrolytes aggregates can be considered as polymeric nanoparticles (Jacquin et al., 2010; Kotz et al., 2001; Raffa et al., 2015). It is worth noticing that nanoparticles flooding is becoming an emerging cEOR technique in relatively recent times (Bera and Belhaj, 2016; Cheraghian and Hendraningrat, 2016a, 2016b; Druetta et al., 2018; Druetta and Picchioni, 2019; Joonaki and Ghanaatian, 2014; Negin et al., 2016).

Associative polymers have been tested in core flood experiments and compared to HPAM, but none of them is structurally similar to the ones studied here, to the best of our knowledge (Bai et al., 2018; Co et al., 2015; Liu et al., 2017; Maia et al., 2009; Yu et al., 2019). Although it is difficult to make comparisons among core flood experiments performed in different laboratories, due to the high operational variability, it is commonly observed that, in opportune optimized conditions, hydrophobically modified polymers can give superior oil displacement. This is due either to better rheological properties, or oil emulsification.

In this work, PS-*b*-PMAA block copolymers previously prepared in our laboratory (Raffa et al., 2013, 2016b), are compared to a commercial HPAM in terms of viscosifying properties, injectivity in filtration tests, emulsification ability, and oil recovered in laboratory scale experiments,

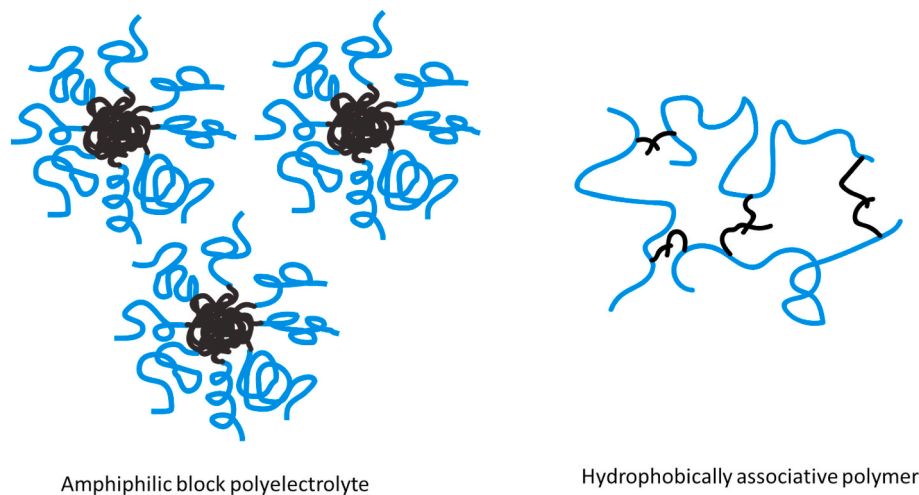


Fig. 1. Different aggregation behavior of amphiphilic block polyelectrolytes and hydrophobically associative polymers in water solution. Blue segments are hydrophilic, black segments are hydrophobic. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

namely bi-dimensional flow cells with dead ends (Klemm et al., 2018; Wever et al., 2013) and flood experiments in a Bentheim sandstone core. Although very preliminary, our results show that amphiphilic block polyelectrolytes can perform better than HPAM in opportune conditions, e.g. low salinity. In this respect, these class of polymers could be proposed for low salinity polymer flooding (LSP). Previous work in LSP shows that this method can potentially perform better than high salinity polymer flooding, because of reduced retention, better long-term injectivity, and better rheological properties, when tested with HPAM in sandstone cores or sand packs (Kakati et al., 2020; Unsal et al., 2018).

Combined with their theoretically higher shear resistance and temperature stability, this makes amphiphilic block polyelectrolytes promising flooding agents.

As a mean to explore the possibility of expanding the application of amphiphilic block polyelectrolytes also for high salinity conditions, a modified version of the polymer, incorporating PEG-acrylate in the hydrophilic block, also designed and prepared in previous work (Raffa et al., 2016b), has been compared to the other systems in terms of viscosity in saline water and emulsification ability. Although the salt tolerance is improved as desired, this polymer performs poorly in filtration tests, therefore it has not been further tested in core flood experiments.

2. Experimental

2.1. Materials

Sodium chloride (NaCl, $\geq 99\%$), toluene (99%), cyclohexane (99%) and glass beads (diameter 425–600 μm), were purchased from Sigma Aldrich. Milli-Q water was used to prepare solutions. Bentheim (D \times L, 5 \times 30 cm) sandstone cores were purchased from Kocurek Industries. Isopore membrane (polycarbonate) hydrophilic filters (pore size = 1.2 and 3.0 μm and a diameter of 47 mm) were purchased from Merck Millipore.

The anionic surfactant Enordet J11111 was kindly supplied by Shell Global Solution International B.V. (the Netherlands).

Partially hydrolyzed polyacrylamide (HPAM) Flopaam 3430 S (10–12 MDa, 25–30% degree of hydrolysis) was kindly provided by SNF Floeger (France).

The amphiphilic block copolymers used in the experiments were synthesized via ATRP followed by hydrolysis and neutralization and characterized in previous work (Raffa et al., 2013, 2016b). PS2MA: triblock polystyrene-b-poly(sodium methacrylate); PS4MA: star block polystyrene-b-poly(sodium methacrylate); PS(PEGA-MA): diblock polystyrene-b-poly(sodium methacrylate-co-PEG-acrylate). More

details, including molecular weight and composition, are given in Table 1.

The crude oil used for the oil recovery experiments was a medium oil (API gravity = 27.8) originated from the Berkel oil field in the southwest of The Netherlands, kindly supplied by Shell Global Solution International B.V. (the Netherlands). It was stored under continuous stirring and its viscosity was adjusted to a value of 90 mPa s at a shear rate of 10 s^{-1} by dilution with cyclohexane before use.

2.2. Rheological characterization

Rheology measurements were performed with a Haake Mars III rotational rheometer with cone and plate geometry, at 20 $^{\circ}\text{C}$.

The solutions were prepared by dissolving the polymers in milliQ water or brine, followed by stirring for at least 10 h before the measurement in order to get homogeneous solutions. All the prepared polymers were soluble in water in their sodium salt form, without the need for co-solvents or heating. The solutions are in general stable for months (no appearance of precipitate or phase separation, reproducible measurements).

2.3. Emulsification tests

Emulsification tests were performed by vigorously shaking manually for 2 min 10 mL solution of polymer at a given concentration (in order to achieve a viscosity of around 100 mPa s at a shear rate of 10 s^{-1}) with 2 mL of crude oil (diluted with cyclohexane to a viscosity of 90 mPa s at a shear rate of 10 s^{-1}). To compare emulsification ability of the polymers, emulsions of polymer solutions at 0.1 wt % with 10 mL of toluene (colored with a drop of oil to improve contrast) were also prepared using the same procedure, and examined with an optical microscope Olympus CX41 equipped with $\times 20$, $\times 40$ and $\times 100$ magnification lenses.

2.4. Flow cell experiments

Flow cell experiments were performed using a 2-dimensional cell with dead ends, consisting of an Aluminum bottom and a transparent plastic top cover, described in our previous work (Klemm et al., 2018; Wever et al., 2013).

For this work another system was designed, constituted by a chamber 250 \times 30 \times 0.5 mm filled with glass beads (diameter 425–600 μm) shown in Fig. 2.

In a typical experiment, the glass beads were inserted from one side of the cell and they were left to settle by gravity. The cell was sealed on both side with a metal mesh to keep the beads in place during flow. The

Table 1

Polymers studied in this work, composition and schematic structure. Grey lines correspond to the hydrophilic blocks and black line corresponds to the hydrophobic polystyrene block. Representation not in scale. AA = Acrylic acid; MAA = methacrylic acid; AM = acrylamide; PEGA = PEG-acrylate.





Name	Molecular weight (Da)	Structure	Composition	Reference synthesis
Flopaam 3430 S	$1,2 \cdot 10^7$		25–30% AA 70–75% AM	–
PS2MA	$6,5 \cdot 10^4$		15% styrene 85% MAA	Raffa et al. (2013)
PS4MA	$1,35 \cdot 10^5$		6% styrene 94% MAA	Raffa et al. (2013)
PS(PEGA-MA)	$4,0 \cdot 10^4$		21% styrene 55% MAA 24% PEGA	Raffa et al. (2016b)



Fig. 2. Device used for flow cell experiments with glass beads (top view).

cell was then filled by flowing an excess of oil (with adjusted viscosity, see description above) at a constant rate of 1 mL/h. Afterwards, brine (0.2 wt % NaCl) was injected through a pump at 1 mL/h for 24 h, followed by polymer solution for additional 24 h at same rate. Pictures were taken at various time intervals.

2.5. Filtration tests

Filtration tests were performed to evaluate the permeation of the different polymer solutions through small pores. The experimental setup used for the filtration tests has been reported elsewhere (Wever et al., 2013).

The device was fitted first with a Millipore polycarbonate filter and subsequently filled with 250 mL of the polymer solution through the top opening. After closing the valves, the cylinder was pressurized to 2 bar with compressed air. The bottom valve was then open and the weight of the effluent collected in a beaker was measured as a function of time using a scale, until more than 200 g of solution has passed. The 2 bar pressure was kept constant throughout the experiment. The ease of passage through the filters was evaluated via a filtration ratio (Fr), calculated using equation (2):

$$Fr = \frac{[t_{200} - t_{180}]}{[t_{40} - t_{20}]} \quad (2)$$

where $t_{200} - t_{180}$ is the throughput time of 20 g of the solution at the end of the test (from 180 to 200 g) and $t_{40} - t_{20}$ is the throughput time of 20 g at the start of the experiment (from 20 to 40 g).

2.6. Core flood experiments

The recovery of oil was evaluated using 5×30 cm Bentheim sandstone cores. The cores were placed in a core holder and saturated with CO_2 . Afterwards, brine (0.2 wt % NaCl) was injected at a low linear velocity (approximately 0.5 m/day) for at least 12 h, to ensure that saturation was reached and no air was introduced (Wever et al., 2013). The core was then filled with oil to connate water saturation and subsequently a water flood was performed until reaching constant water cut (at least 2 pore volumes), followed by polymer flood (at least additional 2 pore volumes) at a linear velocity of 0.3 m/day, which is a typical value for reservoir flooding (Azad and Trivedi, 2018). The pressure drop across the core was recorded during the flooding. Water and oil coming out of the core were collected in test tubes, to measure the volume of oil recovered over time. All the procedures were performed at room temperature.

3. Results and discussion

3.1. Rheology and salt sensitivity

The relevant structural information about the polymers used in this work are summarized in Table 1. They can all be seen as copolymers of acrylic (or methacrylic) acid, therefore as weak polyelectrolytes, but with very different characteristics. Flopaam 3430 S, a commercial HPAM employed in polymer flooding, is a high molecular weight random copolymer of acrylamide and acrylic acid, synthesized by free radical polymerization. The block copolymers were prepared via

sequential ATRP, followed by hydrolysis in previous work (Raffa et al., 2013, 2016b). They are constituted by a hydrophobic polystyrene block and various hydrophilic blocks of pure methacrylic acid (PS2MA and PS4MA) or a statistic block of methacrylic acid and PEG-acrylate, PS (PEGA-MA). As reported above, amphiphilic block copolymers are known to form large spherical micellar aggregates in water solution. Due to the polyelectrolytic nature of the hydrophilic block, the latter are stretched in solution. The aggregates possess therefore high hydrodynamic volume, which is responsible for the viscosifying properties, as the aggregates overlap (Fig. 1). On the other hand, HPAM is present in solution as single chains. Its thickening ability comes from the physical entanglement of chains above the overlapping concentration. Also in this case, the presence of charged units, causes the chains to expand more in solution, with a positive effect on solution viscosity.

A complete rheological characterization of these polymers in water solution, in various conditions of salinity and pH has been already reported (Raffa et al., 2013, 2016b). They show a shear thinning behavior in a large shear rate interval, at concentrations above 0.1 wt %. Interestingly, despite the large difference in molecular weight, the viscosity of the amphiphilic block polyelectrolytes in deionized water is comparable to that of Flopaam 3430 S (Fig. 3), except for PS(PEGA-MA), that requires a concentration 4 times higher. At these concentrations (1–4 wt %), the solutions are thick gels. These concentrations are very high for EOR purposes, but here are used to illustrate that mobility control similar to HPAM can be achieved with amphiphilic block polyelectrolytes, despite their molecular weight being one order of magnitude lower.

The presence of salt has a well-documented negative effect on the viscosity for all polyelectrolytes solutions, as result of contraction of the chains due to screening of charges and osmotic effects (Raffa et al., 2013), with subsequent reduction of the hydrodynamic volume. This is of course a problem for EOR applications, where the used water and the reservoir are usually characterized by high salinity. It is therefore interesting to compare the “damping” effect of salinity on the studied polymers, which possess very different structural characteristics. With this purpose, we measured the shear viscosity of the studied polymers in a NaCl solution (0.5 wt %) and defined a parameter that we called retained viscosity ($\eta_{NaCl\%}$), calculated according to equation (3):

$$\eta_{NaCl\%} = \frac{\eta_{app}(0.5\% \text{ NaCl})}{\eta_{app}(\text{water})} \cdot 100 \quad (3)$$

where η_{app} is the shear viscosity measured at a value of shear of 10 s^{-1} , which is a typical value for EOR processes (Klemm et al., 2018; Wever et al., 2013). It can be note here that the shear rate will not be constant in a porous media, depending on the front location, but we take here an

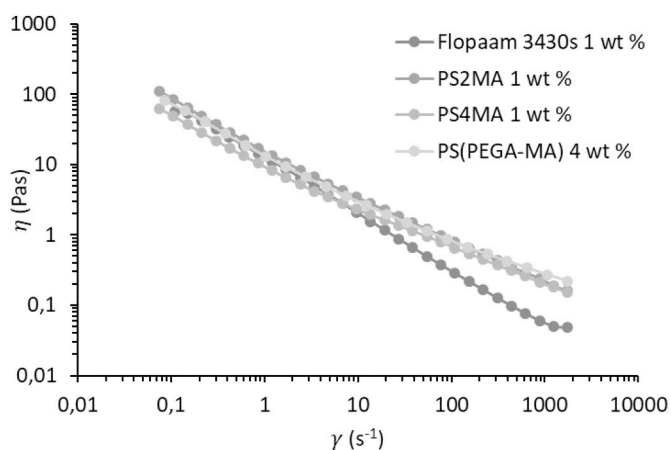


Fig. 3. Shear viscosities (η) in Pa·s as a function of the shear rate (γ) for the studied polymers at high concentration.

average reasonable value. Table 2 reports the obtained values of $\eta_{NaCl\%}$.

It can be observed that the presence of salt has the most negative effect on viscosity for the polymers containing a higher relative percentage of ionized moieties (PS2MA and PS4MA). The different structure (single chains for Flopaam 3430 S and micellar aggregates for the other polymers) and the presence of hydrophobic moieties does not seem to be as significant. PS(PEGA-MA) has the highest retained viscosity at a concentration of 4 wt % (viscosity in water comparable to other polymers), but at the concentration of 1 wt % it behaves very poorly.

3.2. Emulsification experiments

Besides the viscosifying properties and salt tolerance, another aspect relevant for EOR investigated is the ability of the studied polymers to emulsify oil. Although oil emulsification is often seen as a problem in polymer flooding, due to issues in post-extraction processes (Goodarzi and Zendehboudi, 2019), it is also true that formation of emulsion in-situ improves oil mobilization, and therefore increases the yield of oil extracted (Guillen et al., 2012). We are testing here the hypothesis that amphiphilic block polyelectrolytes might help oil recovery not only by mobility control, but also by other mechanisms typical of surfactants. It has been previously observed that PS-b-PMAA block copolymers display negligible surface activity in water (Meijerink et al., 2017), while PS(PEGA-MA) is significantly surface active (Raffa et al., 2016b). The ability of the studied polymers to stabilize an emulsion with crude oil has been tested simply by vigorously shaking solutions of polymer with crude oil. Concentration of polymers (reported in Fig. 4 caption) were chosen in order to have viscosities comparable to the oil. Separation of the phases in the mixtures was then followed over time (Fig. 4). As expected, for Flopaam 3430 S the two phases start separating immediately and separation is nearly complete in 30 min, being slowed down by the relatively high viscosity of the two liquids (Fig. 4a). Remarkably, for the amphiphilic block copolymers no separation is visible for at least 20 h (Fig. 4b, c and 4d), even for PS2MA and PS4MA, which are reported to have negligible effect on surface tension of water. The emulsion stabilization by PS(PEGA-MA) can be explained by the reduced surface tension, which means that this is a true polymeric surfactant. For PS2MA and PS4MA it is more likely that a pickering emulsion is formed, where the polymeric aggregates act as nanoparticles.

To further investigate the emulsification properties, emulsions with toluene in water at various NaCl concentration were prepared and observed with an optical microscope, to have a qualitative evaluation of droplet size (Fig. 5). The toluene phase was colored by adding a drop of crude oil, to increase the contrast with the water phase. The emulsion were prepared by vigorously shaking the two phases, which were then left to settle for 24 h, before observing the emulsified phase (see Fig. 5) at the microscope. For comparison, emulsions with a commercial anionic surfactant (Enordet J11111) were also prepared.

Polymeric surfactants are clearly less effective as emulsifiers, compared to the low-molecular weight Enordet, as evidenced by the lower amount of oil emulsified, and the generally coarser emulsions formed (Fig. 5), with PS(PEGA-MA) performing better than PS2MA. This is in line with the higher surface activity of PS(PEGA-MA) solutions (Raffa et al., 2016b).

Particularly interesting is the behavior observed in presence of salt

Table 2

Retained viscosity values calculated according to equation (2).

Polymer	$\eta_{NaCl\%}$	ionized moieties (M)AA %
Flopaam 3430 S 1 wt %	27.5%	25–30%
PS2MA 1 wt %	9.7%	85%
PS4MA 1 wt %	5.8%	94%
PS(PEGA-MA) 4 wt %	41.3%	55%
PS(PEGA-MA) 1 wt %	2.1%	55%

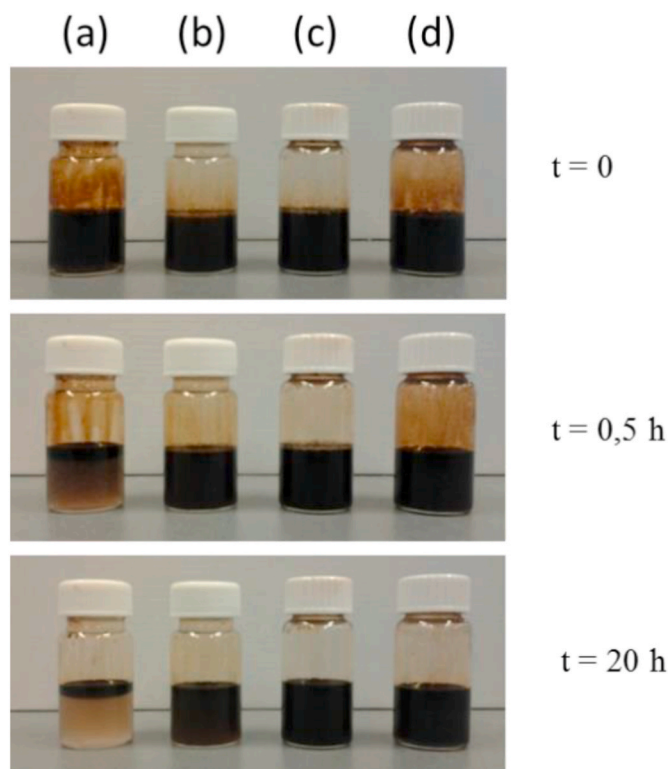


Fig. 4. Emulsification test for the studied polymers: (a) Flopaam 3430 S 0.13 wt%; (b) PS4MA 0.08 wt %; (c) PS2MA 0.1 wt %; PS(PEGA-MA) 0.5 wt %.

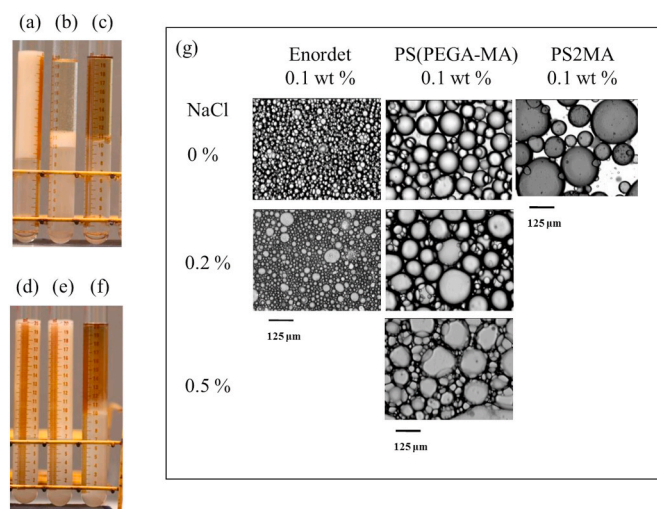


Fig. 5. Emulsions with toluene of: (a) Enordet 0.1 wt %; (b) PS(PEGA-MA) 0.1 wt %; (c) PS2MA 0.1 wt %; (d) PS(PEGA-MA) 0.1 wt % + 0.2 wt % NaCl; (e) PS(PEGA-MA) 0.1 wt % + 0.5 wt % NaCl; (f) PS(PEGA-MA) 0.1 wt % + 2 wt % NaCl and (g) microscope pictures.

for PS(PEGA-MA). Although the droplet size seem to be only marginally influenced by increasing concentrations of NaCl, the amount of toluene emulsified increases for salt concentrations up to 0.5% (Fig. 5d and e), while complete separation and salting out of the polymer is observed for high salinity (2 wt % NaCl, Fig. 5f).

3.3. Flow cells experiments

Flow cells with dead ends of various size were designed and used in previous work (Wever et al., 2013), as a method to evaluate effects of the

viscoelasticity of polymer solutions in oil recovery experiments. In a later work these experiments have been used as a quick screening of microscopic displacement efficiency of polymer solutions (Klemm et al., 2018). Here, we performed analogous experiments with the newly prepared amphiphilic polymers, to have an indication of their performance and highlight possible differences in behavior. The device was filled with crude oil (about 3 mL) and polymer solutions were pushed through the oil from the left side, with a constant flow of 1 mL/h for 24 h. This value is chosen in order to have a value of shear rate in the order of magnitude of 10 s^{-1} (very roughly estimated as $\gamma = 4Q/\pi r^3$, that is used for flow of Newtonian fluids in a pipe). An oil recovery factor has been calculated for various polymer solutions at various concentrations and salinity, based on the swept area in the first 3 chambers of the device, as shown in Fig. 6. The recovery factor (RF) is calculated as the % of the swept area over the total area (pixel count of digital image).

To have a favorable mobility ratio in these experiments, the polymer concentrations were adjusted to a value of viscosity close to the one of the oil (90 mPa s). After flowing polymer solution in the cells for 24 h, pictures for the calculation of RF were taken (Fig. 6). The solution properties and data obtained are summarized in Table 3.

Flow cell experiments do not evidence significant differences in the behavior of the different polymers, with the possible exception of PS (PEGA-MA), that seems to perform slightly worse than other polymers. The only noticeable difference is between polymer flooding and water flooding (Table 3, entry 9). This suggests that in this kind of sweeping experiment, the viscoelasticity is the main factor determining the recovery factor, where the difference in polymer structure does not seem to play a role.

Table 3
Flow cell experiments results.

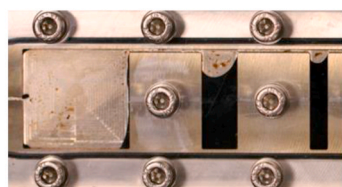
Entry	polymer	concentration %	NaCl wt %	viscosity at shear rate 10 s^{-1} (mPa·s)	RF
1	Flopaam	0.13	–	120	71
2		0.2	0.2	90	76
3		0.2	0.2 ^a	80	87
4		0.35	0.5	100	75
5	PS2MA	0.1	–	120	75
6		0.4	0.2	100	81
7		0.9	0.5	110	71
8	PS(PEGA-MA)	0.25	–	110	65
9	waterflood	–	–	–	39

^a + 0.5% surfactant ENORDET J11111.

In one experiment, Flopaam 3430 S was mixed with a commercial surfactant, to simulate a surfactant-polymer flooding (Table 3, entry 3). It can be noted that the presence of surfactant has a negative effect on viscosity of Flopaam solutions. Despite this fact, the recovery in flow cell experiments is comparable if not better than the one of the polymer alone (Table 3, entry 2), indicating that the reduced interfacial tension positively might affect the recovery in flow cell experiments.

The general conclusion of this set of experiments, is that the amount of oil swept seems to be largely determined by the viscosity of the solution and by some interfacial effect (compare entry 2 with entry 3 in Table 3), but it does not allow to distinguish between different polymeric systems. It can be noted that the flow cell, originally designed to study oil recovery in dead ends to account for viscoelastic effects (Wever

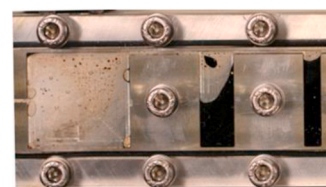
Flopaam 3430 S



0.13 %, no salt
RF = 71 %

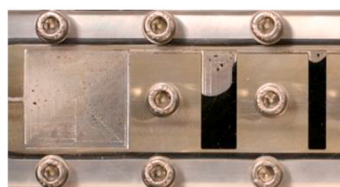


0.2 %, 0.2% NaCl
RF = 76 %

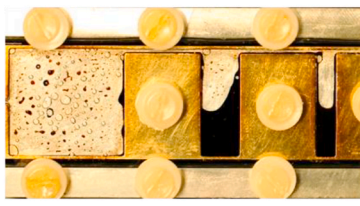


0.35 %, 0.5% NaCl
RF = 75 %

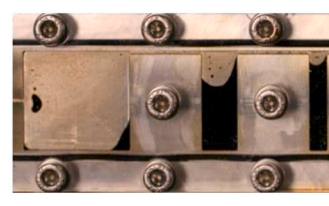
PS2MA



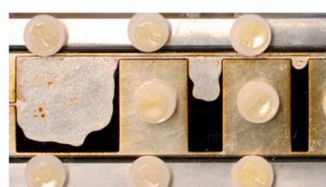
0.1 %, no salt
RF = 75 %



0.4 %, 0.2% NaCl
RF = 81 %



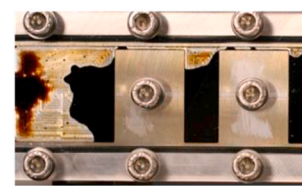
0.9 %, 0.5% NaCl,
RF = 71 %



PEGA
0.25 %, no salt
RF = 65 %



Flopaam
0.2 %, 0.2% NaCl, 0.5 % J
RF = 87 %



water
RF = 39 %

Fig. 6. Flow cell results: Flopaam 3430 S at various concentrations and salinity (top row); PS2MA at various concentrations and salinity (middle row); PEGA, Flopaam + ENORDET J11111 surfactant, water (bottom row).

et al., 2013), it is hardly a realistic representation of the porous rocks present in an oil reservoir, making it not a particularly suitable test for oil recovery.

For this reason, a different system has been designed for this work. An analogous flow cell filled with glass beads was used, to better simulate a porous environment. A picture of the cell and description of the experiment are reported in the experimental section. Flopaam 3430 S and PS2MA were tested with this method and compared. The results are shown in Fig. 7.

Although very qualitative, this test gives some indications on different behavior of the two polymers investigated. The polymer solutions have comparable viscosity (Table 3, entries 2 and 6). The recovery mechanism seems to be different. After water flooding for 24 h in both cells, the solution is switched to polymer. In case of PS2MA a piston-like mechanism is evidenced in the early phase of recovery (1 h), then the polymer solutions keeps pushing out the oil, preferentially from the sides, until the recovery is nearly complete in 6 h. On the other hand, Flopaam 3430 S removes some oil in the first 2 h, leaving large areas unswept, and the recovery does not improve significantly until the end of the experiment at 24 h.

3.4. Filtration tests

To determine the injectivity of the studied polymers, filtration tests were performed through two filters with different pore sizes, respectively of 3 μm and 1.2 μm . A filtration ratio (F_r) close to a value of 1, as defined in the experimental section, indicates good injectivity (Wever et al., 2013). The results are reported in Table 4. Polymer were tested at comparable viscosity (~ 15 mPa s at shear rate of 10 s $^{-1}$). Flopaam 3430 S shows the best injectivity, despite being the polymer with the highest molecular weight. PS2MA possess good injectivity, while the other 2 polymers plug the filter significantly. This suggests that PS4MA and PS (PEGA-MA) might form larger aggregates in solutions, not easily disrupted, or contain insoluble fractions, not visible to the naked eye.

3.5. Core flood experiments

In order to compare a commercial polymer with an amphiphilic block polyelectrolyte prepared in our laboratory, core flood experiments were performed with PS2MA and Flopaam 3430 S solutions on Bentheim cores (5×30 cm), characterized in previous work in terms of porosity, brine permeability and oil saturation (Wever et al., 2013). PS2MA was

Table 4

Filtration tests of the studied polymers.

polymer Concentration	pore size of the filter	F_r
Flopaam 3430 S	3 μm	1.3
0.01 wt %	1.2 μm	1.8
PS2MA	3 μm	1.0
0.04 wt %	1.2 μm	3.3
PS4MA	3 μm	2.3
0.05 wt %	1.2 μm	n ^a
PS(PEGA-MA)	3 μm	n ^a
0.08 wt %	1.2 μm	n ^a

^a n indicates that the filter gets plugged before an amount of 200 g has passed through.

chosen to be the best candidate, based on viscosity measurements and injectivity. PS(PEGA-MA) would be preferred in terms of emulsification ability and viscosity retention in brine, but it has the worst viscosifying properties and, more importantly, bad injectivity, that would cause serious plugging of the core.

As in previous experiments, solutions were prepared in brine (0.2 wt %), at a concentration corresponding to a favorable viscoisty ratio (Table 3, entries 2 and 6). All experiments were conducted at room temperature. The results of the core flood experiments are shown in Fig. 8.

In each experiment, water flooding with brine (0.2 wt %) was first performed for 2 pore volumes. In all cases, this is enough to reach a plateau in oil recovery, corresponding to 40–45% of the initial amount. Then, polymer solution was injected until another plateau was reached. While Flopaam 3430 S is able to recover an additional 5% oil, the amphiphilic block copolymer provides an exceptional incremental recovery, of more than 27% of the initial value, reaching a total recovery of 80%. It is difficult to compare our values with other results reported in literature for core flood experiments, due to the large variability of conditions, oil and rock characteristics, and other factors. A large collection of data recently reported (Saboorian-Jooybari et al., 2016), gives values of incremental recovery of heavy oil in sand packs and sandstone cores after polymer flooding with HPAM in the range 2–35% of the original oil in place.

Pressure drop across the core was measured in the experiments and it was found that for PS2MA this was significantly higher (Fig. 7). Since the two polymer solutions have comparable shear viscosity, this also suggests that some different recovery mechanism can occurs, as already

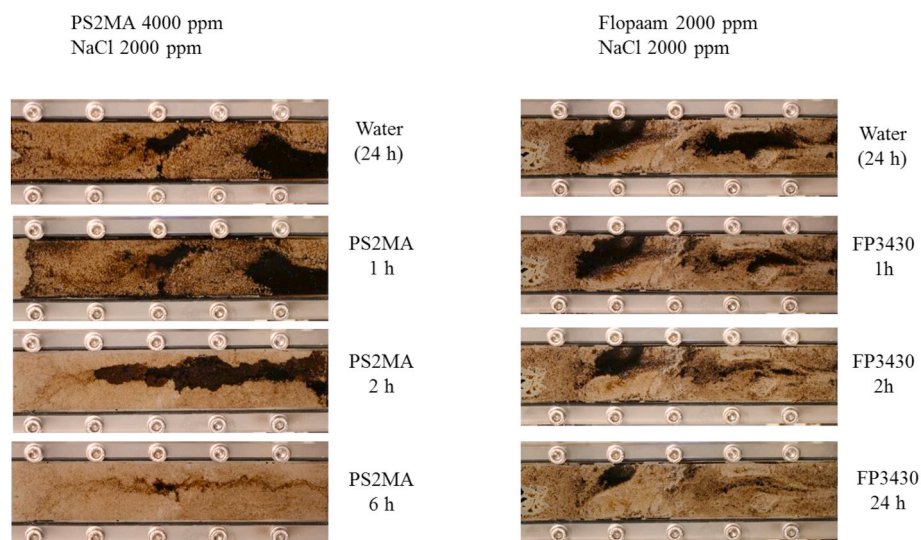


Fig. 7. Flow cell with glass beads experiment (flow is from left to right). The residual oil (black parts) is clearly visible through the glass lid. Before water flooding, the cell looks completely black (not shown).

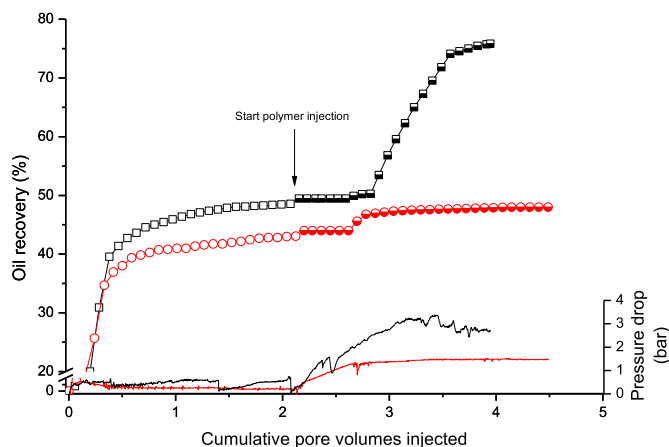


Fig. 8. Core flood experiments at comparable shear viscosity in brine (0.2 wt %): Flopaam 3430 S 0.2 wt % (red line); PS2MA 0.4 wt % (black line). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

evidenced by the flow cell experiments. Increase in pressure drop suggests increase in flow resistance during flooding. This can be due to polymer retention, adsorption or emulsification of the oil. The value of pressure drop stabilizes after about 1 pore volume has been injected. As a result of the higher pressure drop, better sweeping efficiency can result. The high recovery of PS2MA suggests that fingering phenomena are not prevalent in this case. It also has to be noted that the used concentration of polymeric surfactant is double that of Flopaam, which could cause more retention.

It is of interest to test polymers at comparable concentration and pressure drop. Therefore, another experiment was performed with lower concentration of PS2MA (0.2 wt %). In this case, the pressure drop is comparable to that measured for Flopaam (Fig. 8), but still PS2MA is able to recover a higher amount of additional oil after water flooding (incremental recovery of about 9%). It should be noticed here that the viscosity of the PS2MA solution is much lower than that of oil (about 40 mPa s), therefore the viscosity ratio is significantly different for the two compared systems. This might explain also the fact the incremental oil recovery starts with a certain delay (Fig. 9, blue line). This behavior has not been investigated in more depth, but the experiments suggest that a different recovery mechanism is in act.

More insight in these experiments would be given by measuring relative permeabilities, allowing to estimate mobility ratios. It would be

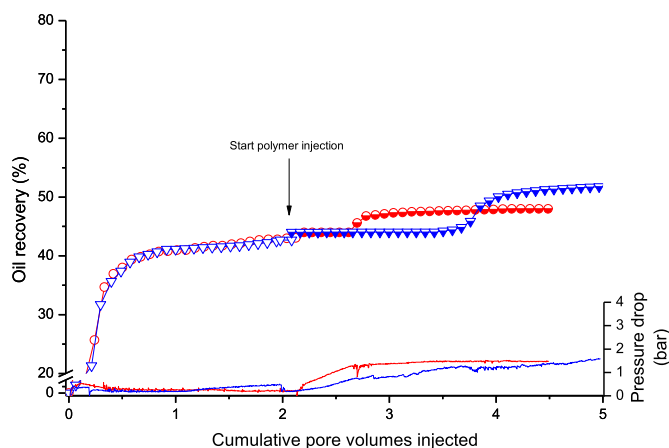


Fig. 9. Core flood experiments at comparable polymer concentration in brine (0.2 wt %): Flopaam 3430 S 0.2 wt % (red line); PS2MA 0.2 wt % (blue line). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

also relevant the measurement of residual oil saturation, by prolonged injection of post-flooding water. In this way, we could investigate if the recovery mechanism is based on recovery of mobile or residual oil in the case of amphiphilic polymers. We thank an anonymous reviewer for bringing our attention to these aspects.

Table 5 summarizes the results obtained with core flood experiments. The rocks used had slightly different values of permeability, which resulted in slightly different values of oil recovered after water flooding (which was stopped when the water cut reached values lower than 1%, corresponding to about 2 PVs). Much higher oil recovery after polymer flooding is measured with PS2MA at 0.4 wt % concentration (27.5%), which is remarkably higher than what obtained with Flopaam at similar shear viscosity. However, this is accompanied by a much higher value of pressure drop (3.5 bar vs 1.5 bar with Flopaam), which might indicate simply a better sweeping of the core with subsequent higher macroscopic displacement. The pressure drop could be due to plugging or emulsion formation, but we can only speculate at this stage.

However, even at comparable values of pressure drop, PS2MA still performs better than Flopaam (9.1% incremental recovery). Remarkably, in this case the viscosity ratio is lower for PS2MA, probably meaning unstable flow. A possible explanation for better recovery at comparable or even lower shear viscosity may be found in considering extensional flow. It has been shown that hydrophobically associating and non-associating polymers possess different extensional viscosity at the same shear viscosity Madhar Sahib Azad et al., 2018a, 2018b. It would be of interest if this applies also to the polymers investigated here.

Overall, the data suggest that a different recovery mechanism is acting in the two processes, not only based on mobility ratio. These findings would require further investigation into the recovery mechanism. In particular relative permeabilities should be estimated, in order to know mobility ratios, and residual oil saturation values could give indication of recovery of residual/trapped oil. Nonetheless, the studied systems prove to be promising flooding agent for oil recovery applications.

4. Conclusions

In this work, PS-b-PMAA amphiphilic block polyelectrolytes are compared to a commercial HPAM (Flopaam 3430 S) in terms of viscosifying properties, injectivity in filtration tests, emulsification ability and oil recovered in laboratory scale experiments, namely bi-dimensional flow cells and flood experiments in Bentheim sandstone cores. To the best of our knowledge, these kinds of polymers were never directly investigated for this purpose.

In this study it is confirmed that these copolymers possess remarkable viscosifying properties, comparable to that of a HPAM of much higher molecular weight, in conditions of low salinity (up to 0.5 wt % of NaCl). The studied polymers also have the characteristics of polymeric surfactants, being able to stabilize emulsions with crude oil, unlike HPAM. Bidimensional flow cell experiments with dead ends do not evidence significant differences among the studied polymers, while cells filled with glass beads suggests better performances of PS2MA over HPAM, and possibly a different recovery mechanism.

PS2MA also shows much better performances than HPAM in core flood experiments in low salinity brine (0.2 wt % NaCl), when the two polymers are tested either at the same concentration or at the same shear viscosity. Our experiments suggest that amphiphilic block copolymers are promising candidates for low salinity polymer flooding (LSP). Based on our results, the oil displacement mechanism seems to be not only based on mobility control, as it is the case for classic polymer flooding. Emulsification might play a role, but further investigations are required to clarify this point, as well as the general recovery mechanism involved. Direct estimation of mobility ratios by measurements of relative permeabilities, and prolonged injection of post-flooding water to determine the residual oil saturation, would certainly be useful in this respect. Nonetheless, our study shows for the first time the potential of

Table 5
Oil recovery experiments.

polymer	Conc (wt %)	η at 10s ⁻¹ (mPa·s)	Core perm. (mD) ^a	Oil recov., brine (% OOIP)	Oil recov., polymer (% OOIP)	Incremental recovery (%)	Pressure drop (bar)
Flopaam	0.2	90	2125	43.0	48.0	5.0	1.5
PS2MA	0.2	40	2125	42.7	51.8	9.1	1.6
PS2MA	0.4	100	2370	48.3	75.8	27.5	3.5

^a Based on values measured in (Wever et al., 2013) for analogous cores.

amphiphilic block polyelectrolytes as flooding agents for enhanced oil recovery, particularly in conditions of low salinity. Further investigations aimed at better evaluate the applicability of such systems in cEOR should include core flood experiments in more realistic reservoir conditions, such as brine containing Ca²⁺ and Mg²⁺ salts, and higher temperatures.

Additionally, in this work, a copolymer including PEG moieties, PS (PEGA-MA), was studied. It shows the best emulsification properties and best salt tolerance, however it possesses very poor injectivity, therefore it was not further investigated in core flood experiments. Optimization of the polymer composition, might provide new systems for high salinity conditions.

Author contributions

Patrizio Raffa: Conceptualization, Methodology, Investigation, Data curation, Writing, Visualization, Francesco Picchioni: Resources, Project Administration, Funding Acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.petrol.2020.108181>.

References

- Abas, N., Kalair, A., Khan, N., 2015. Review of fossil fuels and future energy technologies. *Futures* 69, 31–49. <https://doi.org/10.1016/j.futures.2015.03.003>.
- Afolabi, R.O., Oluyemi, G.F., Officer, S., Ugwu, J.O., 2019. Hydrophobically associating polymers for enhanced oil recovery – Part A: a review on the effects of some key reservoir conditions. *J. Petrol. Sci. Eng.* 180, 681–698. <https://doi.org/10.1016/j.petrol.2019.06.016>.
- Azad, Madhar Sahib, Dalsania, Y., Trivedi, J.J., 2018a. Understanding the flow behaviour of copolymer and associative polymers in porous media using extensional viscosity characterization: effect of hydrophobic association. *Can. J. Chem. Eng.* 96, 2498–2508. <https://doi.org/10.1002/cjce.23169>.
- Azad, Madhar S., Dalsania, Y.K., Trivedi, J.J., 2018b. Capillary breakup extensional rheometry of associative and hydrolyzed polyacrylamide polymers for oil recovery applications. *J. Appl. Polym. Sci.* 135, 46253. <https://doi.org/10.1002/app.46253>.
- Azad, M.S., Trivedi, J.J., 2018. Does Polymer's viscoelasticity influence heavy oil sweep efficiency and injectivity at 1ft/Day? Society of Petroleum Engineers - SPE International Heavy Oil Conference and Exhibition 2018, HOCE 2018. Society of Petroleum Engineers. <https://doi.org/10.2118/193771-MS>.
- Bai, Y., Shang, X., Wang, Z., Zhao, X., 2018. Experimental study on hydrophobically associating hydroxyethyl cellulose flooding system for enhanced oil recovery. *Energy Fuels* 32, 6713–6725. <https://doi.org/10.1021/acs.energyfuels.8b01138>.
- Beliveau, D., 2009. Waterflooding viscous oil reservoirs. SPE Reservoir Evaluation and Engineering. Society of Petroleum Engineers, pp. 689–701. <https://doi.org/10.2118/113132-PA>.
- Bera, A., Belhaj, H., 2016. Application of nanotechnology by means of nanoparticles and nanodispersions in oil recovery - a comprehensive review. *J. Nat. Gas Sci. Eng.* <https://doi.org/10.1016/j.jngse.2016.08.023>.
- Cheraghian, G., Hendraningrat, L., 2016a. A review on applications of nanotechnology in the enhanced oil recovery part A: effects of nanoparticles on interfacial tension. *Int. Nano Lett.* 6, 129–138. <https://doi.org/10.1007/s40089-015-0173-4>.
- Cheraghian, G., Hendraningrat, L., 2016b. A review on applications of nanotechnology in the enhanced oil recovery part B: effects of nanoparticles on flooding. *Int. Nano Lett.* 6, 1–10. <https://doi.org/10.1007/s40089-015-0170-7>.
- Co, L., Zhang, Z., Ma, Q., Watts, G., Zhao, L., Shuler, P.J., Tang, Y., 2015. Evaluation of functionalized polymeric surfactants for EOR applications in the Illinois Basin. *J. Petrol. Sci. Eng.* 134, 167–175. <https://doi.org/10.1016/j.petrol.2015.06.009>.
- Druetta, P., Picchioni, F., 2019. Branched polymers and nanoparticles flooding as separate processes for enhanced oil recovery. *Fuel* 257. <https://doi.org/10.1016/j.fuel.2019.115996>.
- Druetta, P., Raffa, P., Picchioni, F., 2019. Chemical enhanced oil recovery and the role of chemical product design. *Appl. Energy* 252, 113480. <https://doi.org/10.1016/J.APENERGY.2019.113480>.
- Druetta, P., Raffa, P., Picchioni, F., 2018. Plenty of room at the bottom: nanotechnology as solution to an old issue in enhanced oil recovery. *Appl. Sci.* 8, 2596. <https://doi.org/10.3390/app8122596>.
- El-hoshoudy, A.N.N., Desouky, S.E.M.E.M., Elkady, M.Y.Y., Al-Sabagh, A.M.M., Bettiha, M.A.A., Mahmoud, S., 2017. Hydrophobically associated polymers for wettability alteration and enhanced oil recovery – article review. *Egypt. J. Petrol.* 26, 757–762. <https://doi.org/10.1016/j.ejpe.2016.10.008>.
- Goodarzi, F., Zendejboudi, S., 2019. A comprehensive review on emulsions and emulsion stability in chemical and energy industries. *Can. J. Chem. Eng.* 97, 281–309. <https://doi.org/10.1002/cjce.23336>.
- Guillen, V.R., Carvalho, M.S., Alvarado, V., 2012. Pore scale and macroscopic displacement mechanisms in emulsion flooding. *Transport Porous Media* 94, 197–206. <https://doi.org/10.1007/s11242-012-9997-9>.
- Jacquin, M., Muller, P., Cottet, H., Theodoly, O., 2010. Self-Assembly of charged amphiphilic diblock copolymers with insoluble blocks of decreasing hydrophobicity: from kinetically frozen colloids to macrosurfactants. *Langmuir* 26, 18681–18693. <https://doi.org/10.1021/la103391p>.
- Joonaki, E., Ghanaatian, S., 2014. The application of nanofluids for enhanced oil recovery: effects on interfacial tension and coreflooding process. *Petrol. Sci. Technol.* <https://doi.org/10.1080/10916466.2013.855228>.
- Kakati, A., Kumar, G., Sangwai, J.S., 2020. Low salinity polymer flooding: effect on polymer rheology, injectivity, retention, and oil recovery efficiency. *Energy Fuels* 34, 5715–5732. <https://doi.org/10.1021/acs.energyfuels.0c00393>.
- Kamal, M.S., Hussein, I.A., Sultan, A.S., 2017. Review on Surfactant Flooding: Phase Behavior, Retention, IFT, and Field Applications. American Chemical Society. <https://doi.org/10.1021/acs.energyfuels.7b00353>.
- Kamal, M.S., Sultan, A.S., Al-Mubaiyeh, U.A., Hussein, I.A., 2015. Review on polymer flooding: rheology, adsorption, stability, and field applications of various polymer systems. *Polym. Rev.* 55, 491–530. <https://doi.org/10.1080/15583724.2014.982821>.
- Klemm, B., Picchioni, F., Raffa, P., van Mastrigt, F., 2018. Star-like branched polyacrylamides by RAFT polymerization - Part II: performance evaluation in enhanced oil recovery (EOR). *Ind. Eng. Chem. Res.* <https://doi.org/10.1021/acs.iecr.7b03368>.
- Koh, H., Lee, V.B., Pope, G.A., 2018. Experimental investigation of the effect of polymers on residual oil saturation. SPE Journal. Society of Petroleum Engineers, pp. 1–17. <https://doi.org/10.2118/179683-pa>.
- Kotz, J., Kosmella, S., Beitz, T., 2001. Self-assembled polyelectrolyte systems. *Prog. Polym. Sci.* 26, 1199–1232. [https://doi.org/10.1016/S0079-6700\(01\)00016-8](https://doi.org/10.1016/S0079-6700(01)00016-8).
- Lake, L.W., 1989. *Enhanced Oil Recovery*. Prentice Hall, New Jersey.
- Liu, R., Pu, W., Sheng, J.J., Du, D., 2017. Star-like hydrophobically associative polyacrylamide for enhanced oil recovery: comprehensive properties in harsh reservoir conditions. *J. Taiwan Inst. Chem. Eng.* 80, 639–649. <https://doi.org/10.1016/J.JTICE.2017.08.043>.
- Liu, Z., Mendiratta, S., Chen, X., Zhang, J., Li, Y., 2019. Amphiphilic-polymer-assisted hot water flooding toward viscous oil mobilization. *Ind. Eng. Chem. Res.* 58, 16552–16564. <https://doi.org/10.1021/acs.iecr.9b02272>.
- Maia, A.M.S., Borsali, R., Balaban, R.C., 2009. Comparison between a polyacrylamide and a hydrophobically modified polyacrylamide flood in a sandstone core. *Mater.*

- Sci. Eng. C-Biomimetic Supramol. Syst. 29, 505–509. <https://doi.org/10.1016/j.msec.2008.09.018>.
- Meijerink, M., Van Mastrigt, F., Franken, L.E., Stuart, M.C.A., Picchioni, F., Raffa, P., 2017. Triblock copolymers of styrene and sodium methacrylate as smart materials: synthesis and rheological characterization. *Pure Appl. Chem.* 89 <https://doi.org/10.1515/pac-2016-1021>.
- Migliore, N., Picchioni, F., Raffa, P., 2020. The effect of macromolecular structure on the rheology and surface properties of amphiphilic random polystyrene-*b*-R-poly(meth)acrylate copolymers prepared by RDRP. *Soft Matter* 16, 2836–2846. <https://doi.org/10.1039/d0sm00153h>.
- Mohr, S.H., Wang, J., Ellem, G., Ward, J., Giurco, D., 2015. Projection of world fossil fuels by country. *Fuel* 141, 120–135. <https://doi.org/10.1016/j.fuel.2014.10.030>.
- Negin, C., Ali, S., Xie, Q., 2016. Application of nanotechnology for enhancing oil recovery – a review. *Petroleum* 2, 324–333. <https://doi.org/10.1016/J.PETLM.2016.10.002>.
- Nicolai, T., Colombani, O., Chassenieux, C., 2010. Dynamic polymeric micelles versus frozen nanoparticles formed by block copolymers. *Soft Matter* 6, 3111–3118. <https://doi.org/10.1039/b925666k>.
- Raffa, P., Brandenburg, P., Wever, D.A.Z., Broekhuis, A.A., Picchioni, F., 2013. Polystyrene-poly(sodium methacrylate) amphiphilic block copolymers by ATRP: effect of structure, pH, and ionic strength on rheology of aqueous solutions. *Macromolecules* 46, 7106–7111. <https://doi.org/10.1021/ma401453j>.
- Raffa, P., Broekhuis, A.A.A., Picchioni, F., 2016a. Polymeric surfactants for enhanced oil recovery: a review. *J. Petrol. Sci. Eng.* 145, 723–733. <https://doi.org/10.1016/j.petrol.2016.07.007>.
- Raffa, P., Broekhuis, A.A.A., Picchioni, F., 2016b. Amphiphilic copolymers based on PEG-acrylate as surface active water viscosifiers: towards new potential systems for enhanced oil recovery. *J. Appl. Polym. Sci.* 133 <https://doi.org/10.1002/app.44100>.
- Raffa, P., Druetta, P., 2019. *Chemical Enhanced Oil Recovery : Advances in Polymer Flooding and Nanotechnology*. De Gruyter.
- Raffa, P., Stuart, M.C.A., Broekhuis, A.A., Picchioni, F., 2014. The effect of hydrophilic and hydrophobic block length on the rheology of amphiphilic diblock Polystyrene-*b*-Poly(sodium methacrylate) copolymers prepared by ATRP. *J. Colloid Interface Sci.* 428 <https://doi.org/10.1016/j.jcis.2014.04.047>.
- Raffa, P., Wever, D.A.Z., Picchioni, F., Broekhuis, A.A., 2015. Polymeric surfactants: synthesis, properties, and links to applications. *Chem. Rev.* 115 <https://doi.org/10.1021/cr500129h>.
- Saboorian-Jooybari, H., Dejam, M., Chen, Z., 2016. Heavy oil polymer flooding from laboratory core floods to pilot tests and field applications: half-century studies. *J. Petrol. Sci. Eng.* 142, 85–100. <https://doi.org/10.1016/J.PETROL.2016.01.023>.
- Sheng, J.J., 2017. Critical review of alkaline-polymer flooding. *J. Pet. Explor. Prod. Technol.* 7, 147–153. <https://doi.org/10.1007/s13202-016-0239-5>.
- Sheng, J.J., 2010. *Modern Chemical Enhanced Oil Recovery: Theory and Practice*. Elsevier.
- Sheng, J.J., Leonhardt, B., Azri, N., 2015. Status of polymer-flooding technology. *J. Can. Pet. Technol.* 54, 116–126. <https://doi.org/10.2118/174541-PA>.
- Standnes, D.C., Skjevrak, I., 2014. Literature review of implemented polymer field projects. *J. Petrol. Sci. Eng.* 122, 761–775. <https://doi.org/10.1016/J.PETROL.2014.08.024>.
- Su, G., Luo, Y., Li, F., Yu, X., 2019. Preparation and self-assembly properties of surface active hydrophobically associating polyacrylamide. *Geosystem Eng* 22, 30–39. <https://doi.org/10.1080/12269328.2018.1470579>.
- Unsal, E., ten Berge, A.B.G.M., Wever, D.A.Z., 2018. Low salinity polymer flooding: lower polymer retention and improved injectivity. *J. Petrol. Sci. Eng.* 163, 671–682. <https://doi.org/10.1016/j.petrol.2017.10.069>.
- Wei, B., 2016. Advances in polymer flooding. In: El-Amin, M.F.B.T.-V., V, M. (Eds.), *Viscoelastic and Viscoplastic Materials*. InTech, Rijeka. <https://doi.org/10.5772/64069>. Ch. 01.
- Wever, Diego A.Z., Picchioni, F., Broekhuis, A.A., 2013a. Comblike polyacrylamides as flooding agent in enhanced oil recovery. *Ind. Eng. Chem. Res.* 52, 16352–16363. <https://doi.org/10.1021/ie402526k>.
- Wever, D.A.Z., Picchioni, F., Broekhuis, A.A., 2011. Polymers for enhanced oil recovery: a paradigm for structure-property relationship in aqueous solution. *Prog. Polym. Sci.* 36, 1558. <https://doi.org/10.1016/j.progpolymsci.2011.05.006>.
- Yu, F., Jiang, H., Xu, F., Zhen, F., Wang, J., Cheng, B., Su, H., Li, J., 2019. A multi-scale experimental study of hydrophobically-modified polyacrylamide flood and surfactant-polymer flood on enhanced heavy oil recovery. *J. Petrol. Sci. Eng.* 182, 106258. <https://doi.org/10.1016/J.PETROL.2019.106258>.
- Zhang, G., Seright, R.S., 2014. Effect of concentration on HPAM retention in porous media. *SPE J.* <https://doi.org/10.2118/166265-MS>.
- Zhang, H., Xu, K., Ai, H., Chen, D., Xv, L., Chen, M., 2008. Synthesis, characterization and solution properties of hydrophobically modified polyelectrolyte poly(AA-co-TMSPMA). *J. Solut. Chem.* 37, 1137–1148. <https://doi.org/10.1007/s10953-008-9300-4>.
- Zhong, H., Li, Y., Zhang, W., Yin, H., Lu, J., Guo, D., 2018. Microflow mechanism of oil displacement by viscoelastic hydrophobically associating water-soluble polymers in enhanced oil recovery. *Polymers* 10, 628. <https://doi.org/10.3390/polym10060628>.