How to get the best out of hydrophobically associative polymers for IOR? New experimental insights

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Abstract
The associative properties of Hydrophobically Modified Water Soluble Polymers (HMWSP, also called hydrophobically associative polymers) are attractive for IOR, both because of their enhanced thickening capability as compared to classical water soluble polymers (application for mobility control / polymer flooding) and of their marked adsorptions on surfaces (application for well treatments). However, their strong adsorption can obviously impair their injectivity and, conversely, the shear-sensitivity of their gels can be detrimental to well treatments. Determining for which IOR application HMWSP are best suited remains therefore difficult. The aim of this work was to bring new insights regarding the interaction mechanisms between HMWSP and rock matrix and their consequences concerning their propagation in reservoirs.

A consistent set of HMWSP with sulfonated polyacrylamide backbones and alkyl hydrophobic side-chains together with an equivalent WSP were synthesized and fully characterized. HMWSP and WSP solutions were then injected in model granular packs. As expected, with HMWSP, high resistance factors (or mobility reductions, $R_m$) were observed. Yet, within the limit of the injected volumes, the effluent showed the same viscosity and polymer concentration as the injected solutions.

A first significant outcome concerns the specificities of the $R_m$ curves during HMWSP injections. $R_m$ increases took place in two steps: the first corresponded to the propagation of the viscous front, as observed with WSP, whereas the second was markedly delayed, occurring several pore volumes after the breakthrough. This result is not compatible with the classical picture of multilayers adsorption of HMWSP, but suggests that injectivity is controlled by the sole adsorption of minority polymeric species. This hypothesis was confirmed by re-injecting the collected effluents into fresh cores: no second-step $R_m$ increases were observed.

Brine injections in HMWSP treated cores revealed high residual resistance factors (or irreversible permeability reductions, $R_k$) which can be attributed to the presence of thick polymer adsorbed layers on the pore surface. Nevertheless, $R_k$ values strongly decreased when increasing the brine flow rate. This second significant outcome shows that the adsorbed layers thickness is shear-controlled.

These new results should lead to proposing new adapted filtration and injection procedures for HMWSP, aimed in particular at improving their injectivity.

Introduction
A specific attention is devoted nowadays to the development of innovative polymeric systems for IOR applications. The corresponding goals are, in particular: to lower the costs by reducing the quantities of chemicals needed, to broaden the range of suitable application cases (wells or reservoirs) for polymer technologies and, specifically for polymer flooding purposes, to achieve higher recovery factors by taking better advantage of the viscoelastic properties of aqueous polymer solutions. Accordingly, researches on Hydrophobically Modified Water Soluble Polymers (HMWSP, also called hydrophobically associative polymers) receive a renewed interest. HMWSP differ from classical Water Soluble Polymers (WSP) in that they carry low amounts of hydrophobic monomers capable of creating physical associations with each other. Aqueous solutions of HMWSP are well-known within the IOR community to exhibit original steady shear rheological properties as compared to solutions of equivalent WSP, namely: significantly higher viscosities at
low shear rates in semi-diluted regime, higher salt tolerance, lesser sensitivity to mechanical degradation and more marked shear thinning behaviour at high shear rate (Bock J. et al. 1988; McCormick C.L. et al. 1988). Other remarkable properties of HMWSP are the specificities of their interactions with surfaces, since, unlike conventional polymers, their adsorption isotherms do not tend to a plateau when increasing concentration (Argillier J.-F. et al. 1996b; Kim H.S. et al. 2000; Volpert E. et al. 1998b), as well as their ability to form physical gels at high enough concentration (Kujawa P. et al. 2004).

The steady shear rheological properties of HMWSP make them particularly attractive for polymer flooding. Indeed, they can be used, respectively, to reduce the polymer concentration required to achieve a given mobility ratio, to extend the range of suitable reservoirs in terms of salinity and to facilitate the mixing and pumping procedures. As reviewed by Taylor and Nasr-El-Din (Taylor K.C. et al. 1998; Taylor K.C. et al. 2007), experimental studies have been carried out to evaluate the performances in porous media of HMWSP. The major objective of these studies was usually to determine recovery factors from coreflood experiments performed with specific HMWSP, as it is illustrated by the work of Lijian and Biao (Lijian D. et al. 1995), for example. More recently, Buchgraber et al. (Buchgraber M. et al. 2009) have performed a detailed investigation of HMWSP floods in 2D micromodels and have evidenced unexpected displacement patterns, raising stimulating new questions. Nevertheless, rather few publications allow clearly assessing for the injectivity and in-depth propagation of HMWSP for mobility control purposes. The available results (Kun R. et al. 2006; Lu H. et al. 2008; Maia A.M.S et al. 2009) indicate, however, significantly higher resistance factors (or mobility reductions) and residual resistance factors (or permeability reductions) for HMWSP than for corresponding WSP. From the industrial applications side, recent pilot tests carried out by CNOOC in the Bohai Bay offshore field illustrate the potential of HMWSP flooding (Han M. et al. 2006; Liu F. et al. 2008; Wei Z. et al. 2007; Wei Z. et al. 2008), especially in offshore conditions, where strong constraints exist regarding the salinity of the available dissolution brines. A HMWSP test on the Zhongyuan oil field, in central China, has also been mentioned (Wang D. et al. 2008). Yet, to date, detailed reports on HMWSP flooding pilots remain limited to the CNOOC offshore case. On the other hand, the adsorption and physical gel properties of HMWSP have been industrially proved to be useful when applied to water shutoff, conformance control and acid diversion well treatments operations. Detailed reports can be found, in particular, in the works from the group of Eoff, Dalrymple et al. (Eoff L. et al. 2005; Jaripatke O. et al. 2009; Shahan T. et al. 2005; Torres A. et al. 2006), but also in related (Al-Taq A.A. et al. 2007) or distinct (Zhao H. et al. 2010) works.

As can be seen from this brief review, the specific adsorption properties of HMWSP may be useful for well treatments, but can potentially be an issue when mobility control applications are targeted.

The objective of the present work was to investigate the interaction mechanisms between HMWSP and porous rock matrix under dynamic flow conditions, as well as their consequences for HMWSP propagation in reservoirs.

The HMWSP used were composed of sulfonated polyacrylamide backbones, bearing randomly distributed C12 and C18 alkyl hydrophobic side-groups, with various molar fractions. These terpolymers, together with a reference sulfonated polyacrylamide WSP, were synthesized using the micellar radical copolymerization technique and extensively characterized using $^1$HNMR spectroscopy and a newly-developed Micellar Size Exclusion Chromatography (MSEC) technique coupled with Multi-Angle Light Scattering (MALS) (Dupuis G. et al. 2009). The solutions properties of the HMWSP and the reference WSP prepared were then evaluated. Firstly, diluted solutions were characterized in terms of intrinsic viscosity, Huggins constant and colloidal size in solution by Dynamic Light Scattering. Secondly, steady shear rheological properties of semi-diluted solutions were studied in terms of thickening ability versus both concentration and brine’s ionic strength.

Porous media flow experiments were then performed under monophasic conditions with diluted HMWSP and WSP solutions. The option consisting in limiting the investigation to the diluted regime allows uncoupling the specific rheological properties of HMWSP from their other properties, in particular their adsorption. It means that, in the frame of this work, the viscosities of the solutions injected could intentionally not entail by themselves resistance factors values above about 2. The experiments reported here correspond to long-term corefloods (up to a few weeks of HMWSP
injections and up to 130 times the pore volume of the cores) carried out on model granular packs. These corefloods were performed at flow rates representative of typical velocities in-depth the reservoirs. This allowed to assess for HMWSP adsorption as well as to investigate their in-depth propagation.

**Experimental part**

**Synthesis and characterization**

The synthesis conditions and the chemical structure characterizations of the HMWSP and their non-hydrophobic reference WSP investigated in the present study have been presented in details in a previous paper (Dupuis G. et al. 2009), and can be briefly summarized as follows. The full set of polymers was synthesized according to the micellar copolymerization method reviewed by Candau et al. (Candau F. et al. 1999) in which surfactant is used above its critical micellar concentration (cmc) to solubilize the hydrophobic monomers into micelles and ensure their incorporation into the hydrophilic backbone. This process leads to multistickers polymers, namely copolymers with a largely block-like distribution of the hydrophobic units along the hydrophilic backbone. The number of hydrophobic units per block \( N_H \) is assumed to be equal to the number of hydrophobic monomers per micelle. In this study, \( N_H \) was kept constant and equal to one by using surfactant in a large excess. The HMWSP synthesized were partially sulfonated polyacrylamides bearing alkyl chains with various chain length and molar fraction as hydrophobic side-groups. A reference WSP, bearing no hydrophobic units, was synthesized in the same conditions. The detailed chemical structure of the polymers is shown in Erreur ! Source du renvoi introuvable.

![Chemical structure of the HMWSP and the reference WSP used in the study](image)

The molar composition of each polymer was determined by \(^1\text{HNMR}\) (Bruker AVANCE 400MHz). The polymers were dissolved in D\(_2\)O at a concentration of 5 mg/mL. To improve the resolution, all the spectra were recorded at 85°C with a delay time between each pulse of 5 seconds. The purity of the final product was checked. The weight-average molar mass \( M_H \) and the polydispersity index \( (I_p) \) of the samples were determined by using an original Micellar Size Exclusion Chromatography technique coupled to Multi Angle Light Scattering (MSEC-MALS) (Dupuis G. et al. 2009). The results of the molar mass distribution measurements and \(^1\text{HRMN}\) analysis are given in Table 1.

**Polymer samples nomenclature**

The reference WSP is named I20, "I" referring to the presence of AMPS (ionic) and "20" to its AMPS content in molar percent. The HMWSP are named IXCH-Y. "I" mean AMPS (ionic), "X" is the content of AMPS (20 mol-%), "H" refers to the number of carbons in the hydrophobic monomer and "Y" is the content of hydrophobic units in molar percent. For example, I20C12-0.5 is a polymer which contains 79.5 mol-% of acrylamide, 20 mol-% of AMPS and 0.5 mol-% of C12.
**Solution preparation**

Brines and polymers solutions were prepared as follows. "Standard brines" were obtained by dissolution of 20 g/L of NaCl and 400 mg/L of NaN₃ (used as a bactericide) in Milli-Q® water and filtered through 0.22 µm MF Millipore™ membranes. "Stock polymer solutions" were prepared by dissolution of a known amount of polymer powder in standard brine. After 72h of stirring, the solutions were allowed to stand until any bubble disappeared. The concentrations were verified by carbon analysis using a Total Organic Carbon Analyser (TOC-VCSN) from Shimadzu. The solutions were stored at 4°C, over periods of time not exceeding 3 months. Prior to a given experiment, the final desired solution concentration was obtained by diluting the stock solution with standard brine as a regular procedure or with higher or lower salinity brine when needed. Final solutions were allowed to stand during 24h for homogenisation. The concentrations of the final solutions were also verified by carbon analysis.

Prior to the coreflood experiments, the brine and the polymer solutions were carefully degassed under vacuum and kept under a helium cap during the experiments to prevent bubble formation.

**Rheological measurements**

For dilute solutions, the intrinsic viscosity $[\eta]$ and the Huggins constant $k'$ of each polymer were determined in the standard brine according to the Flory-Huggins equation:

$$\frac{\eta_r - 1}{C_r} = [\eta] + k'[\eta] C_r + O(C_r^3) \quad \text{Eq 1}$$

where $\eta_r$ is the Newtonian (zero-shear) relative viscosity of the polymer solution at the concentration $C_r$. Measurements were conducted using a Low-Shear viscometer LS30 from Contraves equipped with a 2T-2T geometry, allowing determining the viscosity of the polymer solution for shear rates ranging from 0.1 to 150 s⁻¹. The polymer concentrations investigated ranged from 0.1 to 2.0 g/L.

The steady shear rheological properties of semi-dilute solutions were determined using a MCR300 rheometer from Physica-Anton-Paar fitted with a Mooney-Ewart geometry (coaxial cylinders with cone and plate at the bottom) in imposed strain mode for shear rates ranging from 0.001 to 500 s⁻¹. Polymer concentrations ranging from 2 to 50 g/L were investigated.

In both cases, dilute and semi-dilute solutions, the temperature was set to 30°C.

**Dynamic light scattering**

Dynamic Light Scattering (DLS) allows determining the hydrodynamic diameter $d_h$ of dispersed particles, namely polymer molecules or polymeric aggregates, with a reasonable accuracy. This technique is based on the fact that the Brownian motion of particles causes the light scattered from the dispersion to fluctuate over time. According to the classical DLS theory (Berne B.J. et al. 2000), the normalized time autocorrelation function of the scattered intensity $g^{(2)}(\tau)$ ($\tau$ being the delay time) is related to the electric field autocorrelation function $g^{(1)}(\tau)$ by a linear relationship (Siegent's relationship). If the size distribution of the dispersed particles is narrow, $g^{(1)}(\tau)$ presents an exponential decay with a decay rate $\Gamma$ proportional to the z-averaged translational diffusion coefficient $D_z$ of the diffusing particles. If the system is sufficiently diluted, the measured $D_z$ represents a correct approximation of the translational diffusion coefficient at infinite dilution, $D_{z,\infty}$, and the particles hydrodynamic diameter $d_h$ is then given by the Stokes-Einstein equation:

$$d_h = \frac{k_B T}{3\pi \eta_s D_{z,\infty}} \quad \text{Eq 2}$$

where $k_B$, $T$, $\eta_s$ are the Boltzmann constant, the absolute temperature and the solvent viscosity respectively. The measurements were performed using a DL-135 from Cordouan Technologies. The polymer concentrations investigated ranged from 0.5 to 2.0 g/L. The temperature was set to 30°C.
Coreflood experiments
The cores used were model granular packs composed of sharp-edged silicon carbide (SiC) grains (from Peter Wolters) having narrow size distribution and average size of 50 µm. Before use, the SiC grains were exposed to chemical and thermal treatment in order to eliminate impurities such as iron particles or fines and to create a thin layer of silica (SiO2) on their surface in order to make the grains hydrophilic (Buret S. et al. 2009; Medout-Marere et al. 2000). Thus, all SiC model porous media used had well-known, homogeneous and reproducible pore structure and surface properties. The experimental setup included an injection system with two constant flow rate piston pumps for injecting brine (Pharmacia P-500) and polymer solutions (Quizix QX6000), respectively, a core holder for the granular pack, a capillary tube of internal diameter \(d_i = 504 \, \mu\text{m}\) and length, \(l = 2 \, \text{m}\) for on-line viscosity measurements and a manometer/pressurization valve system. By mean of two 4-ways valves and a bypass line, the injection system enabled injecting either the brine alone or the polymer solution into either the core with the capillary tube downstream or directly into the capillary tube through the bypass line. The brine route was equipped with a 0.22 µm cellulose MF Millipore TM membrane. In order to remove dusts as well as potential “fisheyes”, all the polymer solutions were pre-filtered prior to each coreflood experiment through a 47 mm track-etched capillary pores polycarbonate membrane with a pore diameter of 3 µm (SPI-Pore TM) and a permeability of 14.1 % at a constant flow rate of 500 mL/h. It is important to indicate here that the coreflood results demonstrate that this pre-filtration stage, at high flow rate, was sufficient to get satisfying injectivity of the reference WSP. As schematically shown on Erreur ! Source du renvoi introuvable., the core holder was equipped with intermediate pressure taps for measurements of the pressure drop on three sections of the 10 cm long and 1.5 cm diameter sand pack. The entrance section (\(E = 0-1 \, \text{cm}\)) enabled checking for front face plugging effects whereas the internal sections (\(S1 = 1-5 \, \text{cm}\) and \(S2 = 5-9 \, \text{cm}\)) enabled investigating the in-depth propagation of the polymers.

![Fig. 2: Schematic representation of the core with its three sections, namely the entrance section (\(E = 0-1 \, \text{cm}\)); the first internal section (\(S1 = 1-5 \, \text{cm}\)); the second internal section (\(S2 = 5-9 \, \text{cm}\)).](image)

The standard experimental procedure included the determination of the porosity (\(\phi\)) and absolute permeability (\(k\)) of the cores, from which the hydrodynamic capillary pore throat radius, \(r_p\), was determined according to a corrected capillary model, i.e. by \(r_p = 1.15 \sqrt{8k/\phi}\), 1.15 being a geometric parameter which has been previously determined (Chauveteau G. 1982). Results indicated a well reproducible pore structure with \(\phi = 41.0 \pm 0.5 \, \%\); \(k = 1000 \pm 100 \, \text{mD}\) and \(r_p = 5.0 \pm 0.5 \, \mu\text{m}\) for all porous media prepared. The injection procedure was designed to get the maximum information on injectivity and permeability damage entailed by the polymers from the measurements of the pressure drops over the different sections of the core as well as over the capillary tube. Its detailed description is as follows: i) reference injection of the brine in both the core (\(\Delta P_B^i, i\) referring to the section, \(E, S1\) or \(S2\)) and the capillary tube (\(\Delta P_B^{capi}\)) at various flow rates and determination of the permeability; ii) injection of the polymer solution at the experiment’s injection flow rate \(Q\) in the capillary tube via the bypass line (\(\Delta P_B^{capi}\), enabling determination of the reference viscosity \(\eta_0 = \Delta P_B^{capi} / \Delta P_B^{capi}\)); iii) injection of the brine in both the core and the capillary tube at \(Q\) to set the baseline pressure drops; iv) injection of the polymer solution at \(Q\) in the core (\(\Delta P_B^i\), enabling determination of the irreversibility permeability reductions) and the downstream capillary tube (\(\Delta P_B^{capi}\), enabling determination of the effluent viscosity \(\eta = \Delta P_B^{capi} / \Delta P_B^{capi}\); v) injection of the brine, at \(Q\) in the first place and then at various flow rates in the core (\(\Delta P_B^i\), enabling determination of the irreversibility permeability reductions). The pressurization valve and the manometer were used between step iv and step v to pressurize the brine’s route at the same pressure than the polymer route.
Mobility and permeability reduction for each core section \(i\), \(R_{m}^{i}\) and \(R_{k}^{i}\), are defined as the ratios of pressure drops during and after the polymer injection respectively, to pressure drops before polymer injection:

\[
R_{m}^{i} = \frac{\Delta P_{m}^{i}}{\Delta P_{m}^{0}} \quad \text{Eq 3}
\]

\[
R_{k}^{i} = \frac{\Delta P_{r}^{i}}{\Delta P_{k}^{0}} \quad \text{Eq 4}
\]

The evolution of the effluent viscosity was monitored by calculating the ratio between the viscosity of the polymer solution flowing through the core and the viscosity of the injected polymer solution, \(\eta/\eta_{0}\):

\[
\eta/\eta_{c} = \frac{\Delta P_{\text{inj}}}{\Delta P_{c}} \quad \text{Eq 5}
\]

If we consider that the permeability impairment is principally due to adsorption on the pore walls, the hydrodynamic thickness of the polymer adsorbed layer on the different sections of the core, \(\varepsilon_{h}^{i}\), can be estimated from the \(R_{k}^{i}\) according to the Poiseuille equation:

\[
\varepsilon_{h}^{i} = r_{p} \left[1 - (R_{k}^{i})^{-1} \right] \quad \text{Eq 6}
\]

The rheological behavior of the adsorbed layers has been investigated as a function of the wall shear rates, which were estimated from the equation:

\[
\gamma = 2.5 \frac{4v}{r_{p}} \quad \text{Eq 7}
\]

where \(v\) is the interstitial mean velocity at the flow rate \(Q\) (\(v = Q/(S\phi)\)), \(S\) being the cross-section of the core and 2.5 a geometric factor which has been previously determined for sharp-edged granular packs (Chauveteau G. 1982; Zitha P.L.J. et al. 2001). As Eq 7 uses the hydrodynamic capillary pore throat radius deduced from the measurement of the core’s initial permeability, i.e. before any polymer injection, it actually allows to determine an initial wall shear rate. After polymer injection, \(r_{p}\) was corrected in order to account for the thickness of the adsorbed layers of polymers on the pore throats walls, leading to an effective hydrodynamic pore throat radius \(r_{p}' = r_{p} - \varepsilon_{h}\). Accordingly, the wall shear rates computed after polymer injection have to be considered as effective wall shear rates and will be noted \(\gamma_{\text{eff}}\) in the following (see "Permeability Reduction" section).

Results and Discussion

Polymers characteristics

**1HNMR molecular composition.** According to previous work (Gouveia L. et al. 2008), the elucidation of the molecular composition of the HMWSPs by careful \(^{1}\text{HNMR}\) measurement allows detecting low content of hydrophobic units. For all the samples, we ensured that the molar composition of the final product corresponded to the molar composition of the feed and that the final purified products were free of unreacted monomers or synthesis residues, namely surfactants.

**MSEC-MALS analysis.** Weight-average molar masses \((M_{w})\) and polydispersity indexes \((I_{p})\) determined by MSEC-MALS are given in Table 1. Considering reasonable experimental uncertainties, the results show that the main chains of each HMWSP as well as the reference WSP had the same weight-average molar, \(M_{w} = (1.2 \pm 0.1) \times 10^{5} \text{ g/mol}\) and polydispersity index, \(I_{p} = 1.8 \pm 0.2\). These verifications were absolutely mandatory in order to perform a meaningful
study of the influence of the nature and amount of hydrophobic monomers on the HMWSP properties.

Table 1: Molecular mass distribution and diluted solution properties of the polymers.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$M_W$ ($10^6$ g/mol)*</th>
<th>$I_P$*</th>
<th>$[\eta]$ (mL/g)</th>
<th>$k'$</th>
<th>$d_h$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I20</td>
<td>1.3</td>
<td>1.8</td>
<td>560</td>
<td>0.4</td>
<td>100</td>
</tr>
<tr>
<td>I20C12-0.1</td>
<td>1.3</td>
<td>1.7</td>
<td>520</td>
<td>0.5</td>
<td>120</td>
</tr>
<tr>
<td>I20C12-0.2</td>
<td>1.3</td>
<td>1.9</td>
<td>600</td>
<td>0.3</td>
<td>120</td>
</tr>
<tr>
<td>I20C12-0.5</td>
<td>1.3</td>
<td>1.8</td>
<td>500</td>
<td>0.5</td>
<td>multimodal</td>
</tr>
<tr>
<td>I20C18-0.5</td>
<td>1.1</td>
<td>1.6</td>
<td>510</td>
<td>1.7</td>
<td>multimodal</td>
</tr>
</tbody>
</table>

* determined by Micellar Size Exclusion Chromatography

Viscosimetric measurements. Results of intrinsic viscosity ([\eta]) and Huggins constant ($k'$) determination carried out in standard brine are shown in Table 1. It appears that for all polymers, the intrinsic viscosity values are identical, namely $[\eta] = 550 \pm 50$ mL/g. As classically stated (De Gennes P.G. 1979), considering that each chain of mass $m_{ch}$ in a diluted polymer solution behaves hydrodynamically like a solid sphere of radius $R$ leads to $[\eta] \sim R^3/m_{ch}$. The intrinsic viscosity hence appears as proportional to the reciprocal of a "density in solution" of the polymers: the lesser $[\eta]$, the "denser", or the less swelled, the polymers. For associative polymers, the intrinsic viscosity is usually supposed to decrease when increasing the hydrophobic content and/or the hydrophobic chain length because of the formation of intrachain bonds between hydrophobic units in the diluted regime (Kujawa P. et al. 2004). Nevertheless, this result is generally reported for HMWSP with high hydrophobic content. In the present case, it is likely that the composition in hydrophobic units is too low ($\leq 0.5$ mol-%) to lead to the formation of significant amounts of intrachain bonds.

Huggins constant values of $0.4 \pm 0.1$, characteristic of good solvent conditions, were obtained for both the reference WSP, I20, and the HMWSP with C12 hydrophobic units. Concerning I20C18-0.5, the $k'$ value above unity ($k' = 1.7$) seems to indicate the existence of marked attractive interactions between the chains or aggregates in solution (this correlation between elevated $k'$ values and attractive interaction, leading to polymer aggregation, has in particular been suggested by Rivenq et al. (Rivenq R.C. et al. 1992)). As a general result from the viscosimetric study in diluted solution, I20C18-0.5 is the only HMWSP to present distinctive properties as compared to the non-associative equivalent WSP, I20.

Dynamic Light Scattering. DLS is a useful tool to identify well-separated bimodal size distribution, but this technique does not easily allow computing size distributions when the sample contains strongly polydisperse species. In this paper, the DLS results are presented under the form of normalized autocorrelation curves, in order to allow a direct and satisfactorily comparison between the polymers studied. These curves were analyzed according to both the Cumulants and the Padé-Laplace algorithms implemented in the software from the manufacturer (Rean™). These automated data analysis methods can provide quantitative size determinations only when monomodal distributions are found.

Since hydrodynamic size determinations by DLS are relevant for sufficiently diluted systems, the concentration dependence of the results was carefully checked for all polymers. Accordingly, the results presented and discussed in the following correspond to 1 g/L polymer concentration. The normalized autocorrelation curves recorded for all polymers at 1 g/L in the standard brine are presented in Figure 1, and the hydrodynamic diameters, $d_h$, obtained from the analysis of these curves are reported in Table 1. It appears that the curves for I20, I20C12-0.1 and I20C12-0.2 can almost be superimposed. For these samples, the data analysis clearly indicated monomodal size distributions, with $d_h$ close to 100 nm for I20 and close to 120 nm for I20C12-0.1 and I20C12-0.2.
Concerning I20C12-0.5 and I20C18-0.5, the normalized autocorrelation curves are markedly different, and the data analysis revealed multimodal distributions. For these samples, a relevant quantitative determination of the size was not possible because the data analysis results were not stable if the delay time scale was varied. This limitation is likely due to the nature of the populations of polymeric particles under study in this work: it reflects the fact that very scattered size distributions of particles actually exists in the diluted solutions in I20C12-0.5 and I20C18-0.5. The only broad conclusions that can be drawn are the following: i) the particle size identified varied from 100 nm to approximately 2 µm, ii) more large objects were identified in I20C18-0.5 than in I20C12-0.5. It should be stressed that the representation in diffused intensity, inherent to DLS technique, strongly emphasizes on the larger sizes. Hence, it is likely that, for both I20C12-0.5 and I20C18-0.5, particles with size in the order of magnitude of 2 µm only correspond to a very limited population in terms of number distribution.

As general results from the diluted regime viscosimetry and DLS study it appears that:
- i) in diluted solutions, I20C12-0.1 and I20C12-0.2 remains under the form of single chains with conformations close to that of the reference polymer I20. For I20C12-0.1 and I20C12-0.2, DLS size measurements are in agreement with the intrinsic viscosity results, indicating similar intrinsic viscosities for these two HMWSP and the reference polymer I20. The results indicate that the presence of some intrachain bonds is not sufficient to impact the hydrodynamic size of 10^6 g/mol and 20 mol-% sulfonated anionic polyacrylamides in 20 g/L NaCl brine.
- ii) multichain aggregates are present in diluted solutions of I20C12-0.5 and I20C18-0.5. Since the corresponding size distributions seem to be rather broad, these aggregates must involve up to a few chains. Since the intrinsic viscosities of I20C12-0.5 and I20C18-0.5 are similar to that of I20, the aggregates must involve both intra and interchain bonds, in order to retain a rather unchanged "density in solution".

**Bulk performances as thickening agents**

The experiments presented in this section aimed at evaluating the bulk performances of the HMWSP as thickening agents in comparison to their equivalent non-associative WSP and at correlating these performances to the diluted solution properties discussed above.

For "classical" WSP solutions, there is a concentration, which depends on the molar mass of the polymer, at which an upward curvature can be observed in the graph of the Newtonian viscosity as a function of the polymer concentration. This upward increase in viscosity is due to the onset of the coil overlap concentration (C*) and is therefore related to the molecular size. A viscosity upturn is also observed in the plots of the Newtonian viscosity of HMWSP versus concentration, but it cannot be attributed to the sole effect of coil overlapping since it usually occurs at a concentration C^‡ close to the C* observed for WSP of similar molar mass. Indeed, for HMWSP, at high enough concentrations, interchain bonds can lead to the formation of an intermolecular physical network,
responsible for a sharp viscosity increase. This viscosity increase is expected to become more pronounced and to occur at lower concentration when the hydrophobic content and/or the hydrophobic chain length increase (Volpert E. et al. 1998a).

The concentration dependence of the Newtonian relative viscosity ($\eta_r$) of the solutions in standard brine at 30°C is shown on Figure 2. Since all polymers are within the same range of molar mass distribution, the results concerning the reference I20 polymer allow determining the coil overlap concentration, $C^*$, namely of about 2.1 g/L. For I20C12-0.1 and I20C12-0.2, no significant difference is observed as compared to I20, even at high concentration. When increasing the hydrophobic content up to 0.5 mol-%, a marked viscosity upturn occurs at a concentration close to $C^*$. This critical concentration can be identified to $C_\eta$, as observed for I20C12-0.5 ($C_\eta^{C12} = 3.2$ g/L) and I20C18-0.5 ($C_\eta^{C18} = 1.3$ g/L). As expected, $C_\eta$ decreases when the hydrophobic unit chain length increase. Comparing these results with the outcomes of the diluted solution study provides interesting new insights for HMWSP made of sulfonated PAM. Indeed the presence of aggregates in diluted solutions of I20C12-0.5 and I20C18-0.5 is related to their enhanced thickening ability, as compared with both the reference WSP (I20) and the HMWSP containing not enough hydrophobic units (I20C12-0.1 and I20C12-0.2) to exhibit distinctive associative properties. Furthermore, these aggregates allow assimilating the transition from diluted solutions to semi-diluted solutions to a sol-gel transition controlled by a percolation mechanism (Adam M. et al. 1996). A detailed study of the properties of the solutions close to $C_\eta$ would be required to further understand the mechanisms responsible for the enhanced thickening ability of the HMWSP. From these viscosimetry results, we decided to perform the diluted regime coreflood experiments at polymer concentrations of 1 g/L, corresponding to Newtonian relative viscosities ranging from 1.5 to 1.9 for the different polymers.

The salt tolerance of HMWSP solutions is a particularly important aspect to assess for nowadays polymer flooding applications, considering the increasing constraints on the available dissolution brines, especially in offshore conditions (Morel D. et al. 2008; Wei Z. et al. 2007; Wei Z. et al. 2008). The viscosity dependences of 5 g/L HMWSP and WSP solutions as a function of the ionic strength are shown in Figure 3. As expected for a WSP, the relative viscosity of I20 decreases when increasing the NaCl concentration due to the screening of the electrostatic repulsions commonly observed for polyelectrolytes. Similar behaviours are observed for I20C12-0.1 and I20C12-0.12, confirming their non-associative behaviour. However, for HMWSP showing clear associating behaviour, namely I20C12-0.5, the relative viscosity first decreases when increasing the NaCl concentration, due to the classical electrostatic repulsion of polyelectrolytes and then increases sharply when further increasing the salinity. This latter behaviour is generally attributed to a reinforcement of the hydrophobic interactions which leads to the formation of a stronger pseudo-gel structure (Feng Y. et al. 2002; Kujawa P. et al. 2006). Similar results were obtained.
with I20C18-0.5 but the results are not shown as it was not possible to reach the Newtonian plateau at this polymer concentration.

![Graph showing Newtonian viscosity vs NaCl concentration, relative to the Newtonian viscosity in "standard brine", i.e. [NaCl] = 20 g/L. Measurements were carried out at a polymer concentration C_P = 5 g/L and at T = 30°C.](image)

As a general result of the study of the bulk performances of HMWSP solutions as thickening agents for IOR and considering their properties in diluted solutions, it appears that:

1. The molar content of hydrophobic units incorporated into the WSP backbone must be at least 0.5 mol-% to lead to a useful thickening ability;
2. The HMWSP with improved thickening ability also present pre-gel aggregates in their diluted solutions.

**Coreflood Experiments**

As stated in the introductory section, the coreflood experiments performed in this study correspond to an investigation of the in-depth propagation and adsorption behavior of solutions of HMWSP and WSP in the diluted regime. This diluted regime option allows evaluating the contribution of the adsorption or retention of the polymers to their injectivity irrespectively of their rheological properties. Accordingly, since the contribution of viscosity (which is the first-order useful parameter for mobility control) to mobility reduction, was fixed for both HMWSP and WSP, reaching high \( R_m \) values was naturally not the objective of this study. In addition, all polymer injections reported in the following were performed at a flow rate \( Q = 2 \) mL/h, corresponding to a Darcy velocity of about 0.3 m/day in our 1.5 cm diameter cores and an initial wall shear rate in the pore throats \( \dot{\gamma} = 15 \) s\(^{-1}\).

**Injectivity of HMWSP vs classical WSP**

In this section, we compare the HMWSP to the reference WSP in terms of injectivity and in-depth propagation, after having performed the sole membrane pre-filtration described in the experimental section.

**General result from effluent analysis.** In order to assess for both transitory and stabilized regimes, large volumes of polymer solutions, representing up to about 130 times the pore volume \( (P_V) \) were injected (with \( P_V \approx 8 \) mL for all experiments, injections lasted for up to a few weeks). For all experiments it appeared that after the polymer breakthrough, which occurred after \( 1.5 P_V \) injected at the maximum, the properties of the effluents were identical to the properties of the injected solution. More precisely, results indicated that for all polymer except I20C18-0.5: i) relative effluent viscosities estimated at shear rates of about 40 s\(^{-1}\) from the capillary tube measurements reached stable values of 100%; ii) Newtonian viscosities of collected effluent samples were identical to the initial viscosities within the uncertainty range of the viscosimeter; iii) polymer concentrations in the effluents were equal to the concentration of the injected solution within the uncertainty range of the carbon analyzer, and iv) DLS correlograms obtained from both injected solution and effluents were superimposed. For I20C18-0.5, namely the more markedly "associative" of the polymers studied, 80% of both the initial viscosity and the initial concentration were recovered, but, as will be discussed in the following, the injection of this polymer had to be stopped prematurely due to the saturation of the pressure sensors measuring the pressure drops.
along the core. Such effluents analyses outcomes indicate that neither significant mechanical degradation, nor conformation modification of the polymer chains occurred during polymer injection. It also means that, regarding the flow in porous media of HMWSP, adsorption or retention does not imply the transfer of significant amounts of polymer from the flowing solution to the porous rock and hence that no significant reduction of the mobility control efficiency of the process should be expected from these phenomena. However, we will see in the following that the limited amounts of material that seem to be involved in adsorption and/or retention are sufficient to provoke marked mobility and permeability reductions.

Reference WSP injection. Figure 4 shows the evolution of the mobility reduction for each section (E, S1 and S2) as well as the evolution of the effluent viscosity (grey curve), obtained during the injection of the reference polymer, I20, in a model granular pack, as a function of the number of injected pore volumes. As classically observed for WSP such as HPAM, the \( R_m \) curves indicate a piston-like propagation of the polymer front, showing stabilization of the mobility reduction. This stabilization corresponds to a \( R_m \) value slightly superior to that of the relative viscosity of the injected solution: this means that a polymer adsorbed layer do form at the surface of the SiC grains. The thickness and the rheological behavior of this adsorbed layer will be discussed in the "Permeability Reduction" section.

HMWSP injection. A dramatically different behavior is observed when injecting a HMWSP having typical "associative" properties. Indeed, during the injection of I20C12-0.5 in a new core (Figure 5), marked \( R_m \) increases are observed (as compared to the Newtonian relative viscosity of the injected solution, \( \eta_0 = 1.7 \)). They take place in two steps: the first corresponds to the propagation of the viscous polymer front as observed with the reference WSP, while the second is markedly delayed as it occurs several pore volumes after the polymer breakthrough. More precisely, during the first three injected pore volumes (Figure 5-a), a classical piston-like propagation is observed on the internal sections S1 and S2 whereas \( R_m \) seems to increase linearly on the entrance face, E. On Figure 5-b, it appears that after 5 \( P_V \) injected, the increase of \( R_m^E \) becomes more pronounced and that, from between 10 and 20 \( P_V \) injected , \( R_m^{S1} \) starts to show a "second-step" increase, while \( R_m^{S2} \) remains stable. After more than about 40 \( P_V \) injected (Figure 5-c), \( R_m^{S2} \) starts "second-step" increasing. Furthermore, results also show that the "second step" increases on all 3 sections are followed by a stabilization trend, tending to \( R_m \) values of the order of about 140 for \( R_m^E \), 100 for \( R_m^{S1} \) and more than 50 for \( R_m^{S2} \). The repeatability of these results was checked, as shown on Figure 5-d, presenting the superposition of the \( R_m \) curves obtained for the injection of three different solutions of I20C12-0.5 in three different fresh cores.

The stabilization trends observed on the \( R_m \) curves are consistent with the effluent viscosity \( \eta / \eta_0 \) (grey curves) indicating that almost 100% of the injected polymers are able to flow through the porous medium and, more generally, with the outcomes of the effluent analysis.
It seems clear that such elevated $R_m$ values, while injecting rather low viscosity solutions, are linked to marked permeability reduction effects caused by either pore-throat size reduction due to polymer adsorption or by steric pore-blocking due to large aggregates. Accordingly, the progressive "second-step" increases in $R_m$ can be associated to the propagation of a permeability impairment front. At this point, this naturally, does not imply making any assumption regarding the reversible or irreversible nature of these permeability reductions.

A detailed interpretation of these results is however not straightforward. In particular, the classical mechanism associated with the surface adsorption of HMWSP, namely the formation of multilayers mediated by hydrophobic interchain interactions (Argillier J.-F. et al. 1996a; Volpert E. et al. 1998b), does not seem compatible with the fact that the permeability impairment front propagates very slowly along the core, while the effluent analysis indicates that after not more than about 2 $P_V$ injected, almost 100% of the injected polymers flow through the whole core. It seems more likely that the slow propagation of the permeability impairment front is caused by the sole adsorption or steric pore-blocking of specific polymeric species which are minority enough not to contribute to the viscosity of the solution. According to this picture, all minority species that are required, on a section "n" of the core, to achieve the high permeability reduction up to the stabilized $R_m$ values need to be consumed before the high permeability reduction front reaches section "n+1". This hypothesis allows understanding why the permeability impairment front propagates so slowly.

The minority species could likely be the pre-gel aggregates identified from the DLS measurements. However, as a result, the DLS autocorrelation curves obtained from both the injected solution and from the effluents collected throughout the experiment can always be superimposed. This observation evidences for the continuous presence of pre-gel aggregates in the effluents, from the initial breakthrough. Thus, in order to propose an interpretation that agrees with the entirety of the experimental results, it is necessary to suggest that either only some HMWSP are able to create multilayers of adsorbed polymers, or that only some of the pre-gel
aggregates are able to adsorb on the rock surface or to cause steric pore blocking. In both cases, the hypothesis of minority species responsible for the propagation of the permeability impairment front can easily be checked. A relevant test can indeed be performed by re-injecting effluents collected before the onset of the "second-step" $R_m$ increase trend on the S2 section of the core. This test will be presented and discussed in the section "optimization of the HMWSP filtration procedure".

**Impact of the chemical composition.** Figure 6 presents the results of 4 different corefloods, corresponding respectively to the injection of diluted (1 g/L) solutions of polymers I20, I20C12-0.2, I20C12-0.5 and I20C18-0.5 in distinct fresh cores with the same petrophysical properties. Since the results were the same for all sections of the cores, all $R_m$ curves shown correspond to the first internal section, S1 (1-5cm). For I20C12-0.2, no different behavior from the reference WSP is observed, as the $R_m$ curves for I20 and I20C12-0.2 can be superimposed (in the limit of the number of $P_V$ injected). For I20C18-0.5, the qualitative behavior is similar to that observed for I20C12-0.5, meaning that the $R_m$ increase occurs in two steps, with an onset of the "second-step" increase taking place between about 10 and 20 injected $P_V$. However, the $R_m$ values reached with I20C18-0.5 are much higher than those reached with I20C12-0.5. Unfortunately, saturation of the differential pressure transducers occurred when mobility reduction on section S1 reached a value of about 2000 (not shown on the plot in order to allow a clear comparison with the other polymers) and the injection had to be stopped. Thus, although an inflexion was observed on the slope of the $R_m^{S1}$ curve, the stabilization trend was not properly observed for I20C18-0.5. However, as previously stated, the effluent analysis did not indicate very strong polymer retention, at least in the limit of the volume of the polymer solution injected. Indeed, starting from about 20 $P_V$ injected, effluent viscosity and concentration corresponded to 80% of the viscosity and the concentration of the injected solution and did not show a decreasing trend. For these reasons, it appears that, qualitatively, the same mechanism based on the propagation of a permeability impairment front caused by "minority species" can be proposed to interpret the result obtained for both I20C12-0.5 and I20C18-0.5.

**Optimization of the HMWSP filtration procedure**

The previous results show that even diluted solutions of HMWSP can entail very high in-depth mobility reductions, with values about two orders of magnitude above the Newtonian relative

![Figure 6: Impact of the chemical composition on the injectivity of HMWSP compared to the reference WSP. Injections of diluted solutions of I20, I20C12-0.2, I20C12-0.5 and I20C18-0.5 at $Q = 2$ mL/h in distinct fresh cores with the same petrophysical properties. The $R_m$ curves represented correspond to the first internal section, S1, of the cores. Solutions were pre-filtered on 3 µm pore size membranes at 500 mL/h.](image)

Furthermore, the fact that much higher mobility reductions are obtained for I20C18-0.5 than for I20C12-0.5 is consistent with both the much more marked thickening ability of I20C18-0.5. In addition, although the results do not allow proposing any further assumption regarding the nature of the minority species, it is worth reminding here that the DLS autocorrelation curve for I20C18-0.5 indicated the presence of larger aggregates in solution than for I20C12-0.5. Similarly, the fact that I20C12-0.2 behaves exactly as I20 is also consistent with the viscosimetric and DLS study.

**Optimization of the HMWSP filtration procedure**

The previous results show that even diluted solutions of HMWSP can entail very high in-depth mobility reductions, with values about two orders of magnitude above the Newtonian relative
viscosity of the solutions. If these mobility reductions can translate into irreversible permeability modifications, this means that HMWSP might be useful as well treatment agents. These aspects will be discussed in the section "Permeability Reduction". However, for sole mobility control purposes, mobility reduction should not significantly exceed the Newtonian relative viscosity, in order, notably, to ensure a good injectivity of the polymers. In this section, we discuss the optimization of the filtration procedures for HMWSP with the purpose of achieving mobility reductions as close as possible to those obtained with the reference WSP. We will also see how the hypothesis of minority species, responsible for the high mobility reductions, can be tested.

**Re-injection tests.** The coreflood experiments discussed above were performed by injecting solutions that had previously been submitted to a rather coarse pre-filtration, carried out on track-etched capillary pore polycarbonate membranes with a pore diameter of 3 µm at a high flow rate of 500 mL/h. This pre-filtration was aimed at eliminating dusts and impurities such as non soluble particles or fisheyes that can be present in any polymer solution. The coreflood tests have clearly shown that such pre-filtration was sufficient to ensure a very good injectivity for the reference WSP as well as for the weakly associative polymer I20C12-0.2. Conversely, the results obtained from the experiments carried out with I20C12-0.5 and I20C18-0.5 indicated very high permeability reductions and were consistent with the possibility of adsorption or pore-blocking caused by minority polymeric species, entailing the slow propagation of a permeability impairment front. Such mechanism implies that the effluents collected downstream the core from the polymer breakthrough to the onset of $R_m^{S2}$ increase should be free of the damaging minority species. In order to trial this hypothesis, we re-injected into fresh cores the effluents collected under the latter condition.

The corresponding $R_m^{S1}$ results for the re-injection experiments of I20C12-0.5 and I20C18-0.5 are reported in Figure 7 (2nd injections), together with the results of the initial injection of these two HMWSP (1st injections) as well as those of the reference WSP, I20. Obviously, the mobility reduction curves trends are dramatically different for the 1st than for the 2nd injections. More precisely, during the 2nd injections, $R_m^{S1}$ values reached are close to the Newtonian relative viscosities of the injected solutions i.e. close to the $R_m^{S1}$ of the reference WSP and much lower than the $R_m^{S1}$ values obtained for the 1st injections, at the same number of PV injected. Hence, as a result, the re-injected HMWSP solutions do appear to be free of the minority species causing marked permeability impairments. It also appears that the $R_m^{S1}$ curve for the 2nd injection of I20C18-0.5 shows a slight increasing trend. This seems to indicate that some of the damaging minority species remain in the re-injected solution. Accordingly, achieving an optimal injectivity for I20C18-0.5 should imply using either a longer core, or collecting lesser effluent for re-injection.
of the collected effluent solution of I20C12-0.5 intended for the 2nd injection was precipitated in ethanol, dried, and used to prepare new semi-diluted solutions in standard brine on which viscosity measurements were performed. The corresponding results are presented in Figure 8, and compared with the Newtonian relative viscosity vs concentration values determined for the I20C12-0.5 solution that was used for the 1st injection. The two plots can be superimposed: the two HMWSP solutions have thus the same thickening ability. This means that the minority species retained in the first porous medium are not responsible for the associative behavior of the HMWSP. Further investigations are underway to determine the exact nature of these minority species, by considering in particular the control, through the synthesis process, of the repartition of the hydrophobic units along the hydrophilic backbone.

Figure 8: Newtonian relative viscosity ($\eta_r$) vs polymer concentration (C) of solutions of the I20C12-0.5 polymer sample used for the initial coreflood (1st injection) and the effluent re-injection coreflood (2nd injection). The thickening ability of the HMWSP is preserved. Measurements were carried out at 30°C in "standard brine".

Comparison between membrane and porous medium pre-filtration. The results presented above show that an additional pre-filtration at low flow rate on a porous medium (following the initial membrane filtration at 500 mL/h) is a particularly efficient way to achieve a good injectivity of HMWSP solutions. It is however not sure that this kind of process would always be feasible at a large scale. For this reason, we have also investigated the effect of a second membrane pre-filtration, performed on a fresh 3 µm capillary pore membrane, at a low flow rate of 2 mL/h.

Figure 9 presents the $R_m^{ST}$ curve obtained from a coreflood test performed with an I20C12-0.5 solution pre-filtered twice on distinct membranes, first at a flow rate of 500 mL/h and second at 2 mL/h (F500-F2). On the same Figure are also shown the $R_m^{ST}$ curves obtained for coreflood tests performed with solutions of the same polymer after the sole 500 mL/h pre-filtration (F500) and after the 500 mL/h pre-filtration followed by the "porous medium" pre-filtration carried out at 2 mL/h (F500-MP2) as described in the previous section. It clearly appears from the plots that adding a second filtration at low flow rate allows significantly enhancing the mobility reduction control. Indeed, for the F500-F2 experiment, $R_m^{ST}$ is kept rather close to the value of the Newtonian relative viscosity up to 21 $P_v$ injected. However, a continuous increasing trend of $R_m^{ST}$ is observed for this experiment, while it is obviously not the case for the $R_m^{ST}$ corresponding to F500-MP2. Low flow rate pre-filtration on a membrane is thus not completely equivalent to a core pre-filtration for removing the minority polymeric species. Polymer injections at higher flow rates should nevertheless be performed in order to assess whether membrane pre-filtrations could be sufficient to ensure a satisfactorily injectivity of the HMWSP.
Figure 9: Impact of the pre-filtration procedure on mobility reductions entailed by HMWSP injections. $R_m$ determined for injections in distinct cores with the same petrophysical properties of solutions of I2OC12-0.5 pre-filtered once on a membrane at 500 mL/h (F500), pre-filtered twice on distinct membranes at 500 mL/h and 2 mL/h (F500-F2) and pre-filtered once on a membrane at 500 mL/h and once in a core at 2 mL/h (F500-MP2). The coreflood experiments were all performed at $Q = 2$ mL/h; all polymer solutions had concentration $c_p = 1$ g/L and Newtonian relative viscosities $\eta_r = 1.7$.

To summarize, it appears from these corefloods results that, if no specific care is dedicated to the pre-filtration of HMWSP as compared to regular WSP, marked in-depth permeability impairment can occur, entailing abnormally high mobility reductions which are potentially detrimental to HMWSP injectivity. Nevertheless, the results show that it is possible to design adapted pre-filtration procedure to ensure well controlled HMWSP injectivity, without degrading their enhanced performances as thickening agents.

**Permeability Reduction**

Permeability reduction after injection of the reference WSP. As described in the "Experimental part" section, the irreversible permeability reductions have been studied after the polymer injections by injecting large brine volumes at different flow rates. This allowed to directly determine the irreversible permeability reduction, $R_k$, from which the thickness of the polymer adsorbed layer, $\varepsilon_h$, can classically be computed as a function of the effective wall shear rate $\dot{\gamma}$

It should be stressed here that numerous previous works have shown that polymer adsorption on porous rock surface could reasonably be considered as almost "irreversible" (Chauveteau G. et al. 1991), even on extended time scales.

$R_k$ and $\varepsilon_h$ results obtained the reference WSP, I2O, are shown on Figure 10. Since these results were the same over all the 3 sections of the core, the data shown are limited to the S1 section. The flow rates investigated ranged from 2 mL/h to 64 mL/h in a first step, and then from 64 mL/h to 2 mL/h in a second step, in order to check for possible hysteresis effects. These flow rates corresponded to $\dot{\gamma}$ ranging from 15 s$^{-1}$ to 550 s$^{-1}$. The results indicate a stable $R_k$ value of 1.20 and a stable $\varepsilon_h$ value of 0.25 µm. The thickness of the polymer adsorbed layer is hence higher than the hydrodynamic diameter of 0.1 µm determined for the I2O chains by DLS. Since there is no specific reason for any attractive interactions between the chains, it seems reasonable to assume that the polymers were adsorbed as a very compact monolayer and that steric repulsions have entailed some conformation change of the chains. Moreover, as a result, no shear thickening effects are observed, whereas these kind of phenomena have been clearly reported for polymer adsorbed layer rheology investigations carried out in granular porous media in which extensional shear deformations are present (Bagassi M. et al. 1989). The reason for this could lie in the fact the polymers adsorbed as a compact monolayer are already in a rather stretched conformation, which implies that no further shear-induced coiled-to-stretched conformation transition can be expected. These specific behaviors could be linked with the rather low molecular weight of the polymers studied ($M_w = 1.3 \times 10^6$ g/mol), as compared to regular EOR polymers, and is undoubtedly worth carrying out more detailed investigations. However, the primary objective in this paper is to
compare a reference WSP with HMWSP, and we will see in the following that the adsorbed layer thicknesses obtained with HMWSP are drastically different as the ones discussed in this section.

Figure 10: Investigation of the dependence of the irreversible permeability reduction on section S1 of a core ($R_k^{S1}$) and of the polymer adsorbed layer thickness ($\varepsilon_{h}^{S1}$) versus the effective wall shear rate ($\dot{\gamma}^{\text{eff}}$) after injection of a solution of the reference WSP, I20, as shown on Figure 4. The stable $\varepsilon_{h}$ value of 0.25 µm is of the order of the hydrodynamic diameter of the I20 chains determined by DLS (see text).

**Permeability reduction from HMWSP injection.** For HMWSP, the irreversible permeability reduction effects have been studied after the injection of a 1 g/L solution of I20C12-0.5 pre-filtered once on a 3 µm capillary pores membrane at 500 mL/h. The objective was to investigate the shear-rate dependence of the permeability reduction, namely its robustness in view of well-treatments operations. We have performed qualitatively similar brine injections at various flow rates as with the reference WSP.

As a striking difference as compared to WSP, the pressure drops during these brine injections were not stable versus time. As shown in Figure 11 (a), during stepwise increases of the brine flow rates, the pressure drops decrease significantly and tend to plateau values. Furthermore, during stepwise decreases of the brine flow rate, Figure 11 (b), the pressure drops show slight increasing trends, also tending to plateau values. In order to propose an interpretation for this behavior, it is necessary to first discuss the evolution of the measured plateau values of $R_k$ versus the effective wall shear rates investigated.

The corresponding results are shown on Figure 12 for the section S1 of the core, the various brine flow rates investigated being translated into effective wall shear rates $\dot{\gamma}^{\text{eff}}$. The brine injections were performed according to a long term (up to more than 1 month) 3-cycles procedure. During each cycle, the brine flow rate was increased from an initial value of 2 mL/h to a maximum value of 8, 64 or 128 mL/h, respectively for cycle 1, 2 and 3, and then decreased to 2 mL/h. The same flow rates were investigated during the increasing and decreasing steps. Between cycle 1 and cycle 2 the flow rate has been set to zero for 72 h.
Figure 12: Investigation of the dependence of the irreversible permeability reduction on section S1 of a core \( R_{k}^{S1} \) and of the polymer adsorbed layer thickness \( \varepsilon_{h}^{S1} \) versus the effective wall shear rate \( \dot{\gamma}_{\text{eff}} \) after injection of an I20C12-0.5 solution as shown on Figure 7-c. Three cycles of stepwise increase and decrease of the brine flow rate have been investigated. \( R_{k}^{S1} \) and \( \varepsilon_{h}^{S1} \) appear to be controlled by the maximum effective wall shear rate applied.

As a first observation, it appears that the \( R_{k}^{S1} \) values range between about 50 to about 5, namely much higher values than those obtained for the WSP. Thus, as a result, the marked permeability reductions corresponding to the high \( R_{m} \) values reached during HMWSP injection, appear to be, to a significant extend, irreversible effects.

Polymer adsorbed layer thicknesses, \( \varepsilon_{h}^{S1} \), were computed from \( R_{k}^{S1} \). Although these \( \varepsilon_{h}^{S1} \) values are much higher than those obtained with the WSP (a few µm versus 0.25 µm), they always remain more than 2 µm lower than the initial capillary pore throat radius \( r_{P} \approx 5 \mu m \). This means that, after polymer adsorption, more that half the pore throats remain open for fluid flow. In addition, although the DLS results evidence for large particles in the injected solutions, the presence of significant enough amounts of those particles to entail steric bridging or pore blocking effects do not seem likely, especially in-depth the core. Hence, we propose to interpret the irreversible permeability reduction effects as being mainly caused by the formation of a thick polymer adsorbed layer of HMWSP on the pore throat walls. In spite of the fact that, on the basis of our investigations, it is not possible to determine the nature of the minority polymeric species responsible for the high permeability reduction, it is likely that this adsorbed layer can be assimilated to a gel phase, composed of assemblies of HMWSP chains with numerous intra and interchains hydrophobic bonds.

As a second major outcome, the \( R_{k}^{S1} \) values strongly decrease when increasing the effective wall shear rate. More precisely, it appears that the \( R_{k}^{S1} \) and \( \varepsilon_{h}^{S1} \) values obtained at the maximum \( \dot{\gamma}_{\text{eff}} \) of cycle 1 are the same than those obtained at the same \( \dot{\gamma}_{\text{eff}} \) during cycle 2, and that the same observation can be made between cycle 2 and cycle 3. The \( R_{k}^{S1} \) and \( \varepsilon_{h}^{S1} \) values are hence limited by the maximum \( \dot{\gamma}_{\text{eff}} \) investigated, which also naturally corresponds to the maximum stress applied on the adsorbed layer. Furthermore, when decreasing \( \dot{\gamma}_{\text{eff}} \), the result show limited increases of \( R_{k}^{S1} \) and \( \varepsilon_{h}^{S1} \).

The decrease in \( R_{k}^{S1} \) and \( \varepsilon_{h}^{S1} \), which are observed both versus time at a given \( \dot{\gamma}_{\text{eff}} \) and from the plateau values when increasing \( \dot{\gamma}_{\text{eff}} \), can be due either to polymer desorption or to conformation changes. Although the relative contributions of these two mechanisms cannot be quantitatively assessed, conformation changes are likely to occur as they can correspond to the formation of additional hydrophobic bonds between the chains in the gel layer. Indeed, the life time that is classically associated to the hydrophobic bonds in physical gels can be increased by applying more stress on the gel layer. This hypothesis is also consistent with i) the slight \( R_{k}^{S1} \) and \( \varepsilon_{h}^{S1} \) increases observed from the plateau values when decreasing \( \dot{\gamma}_{\text{eff}} \), ii) the \( R_{k}^{S1} \) increases observed versus time at each \( \dot{\gamma}_{\text{eff}} \) when \( \dot{\gamma}_{\text{eff}} \) is stepwise decreased and iii) the notable increase of
$R_{k}^{S1}$ and $e_{h}^{S1}$ observed between the end of cycle 1 and the beginning of cycle 2, while no stress is applied on the gel layer.

From a practical point of view, our results demonstrate that for well treatments operations purposes, water permeability control can be achieved with diluted solutions of the HMWSP investigated. However, the water flow rates to which the treated layer are to be exposed, need to be carefully assessed.

Conclusion
The main outcomes of this work can be summarized as follows:

1. Moderate molecular weight (c.a. $10^6$ g/mol) HMWSP synthesized by micellar copolymerization and consisting of sulfonated polyacrylamide backbones bearing randomly distributed alkyl hydrophobic side groups present strongly enhanced thickening ability as compared to reference WSP;

2. Long-term injections of diluted solutions of these HMWSP in porous media under monophasic conditions reveal markedly different behavior as compared to reference WSP. Indeed, the mobility reductions reached with HMWSP are significantly higher than the viscosity of the injected solution. Yet early polymer breakthrough and stable composition of the effluents are observed. This behavior could potentially be detrimental to injectivity;

3. The high mobility reductions observed with HMWSP are due to the adsorption/retention of minority polymeric species. These minority species can be removed from the solutions by means of proper filtration procedures, without degrading the thickening ability of the polymers. If a practical large-scale filtration method can be found that removes the minority species, the HMWSP studied could be useful for mobility control applications;

4. HMWSP coreflood results also indicate marked irreversible permeability reductions when no specific filtration is performed. These effects could be linked to the formation of thick layers of physical gel adsorbed on the pore throats. Permeability reductions values are controlled by the maximal shear applied when injecting brine in the HMWSP treated core. Such behavior could be exploited for water permeability reduction purposes in well treatments operations.

Future works on these HMWSP will focus on coreflood studies under semi-diluted conditions at various injection flow rates. In addition, the potential benefit in terms of mechanical degradation of the low molecular weight of the HMWSP as compared to regular EOR WSP, will be quantitatively studied.

Furthermore, it is worth stressing that HMWSP with potentially much more marked associative properties can easily be produced from the micellar copolymerization technique, by increasing $N_{hi}$, the number of hydrophobic monomers per block along the polymer backbone (Bastiat G. et al. 2005). Investigations of the detailed thickening ability and salt tolerance of such HMWSP, as well as their behavior in porous media are planned.

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Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
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</thead>
<tbody>
<tr>
<td>$I_p$</td>
<td>Polydispersity index</td>
</tr>
<tr>
<td>$M_W$</td>
<td>Weight average molar mass [g/mol]</td>
</tr>
<tr>
<td>$C_F$</td>
<td>Polymer concentration [g/L]</td>
</tr>
</tbody>
</table>
Intrinsic viscosity [mL/g] \( \eta \)

Huggins constant \( k' \)

Hydrodynamic diameter [\( \mu m \)] \( d_h \)

Relative Newtonian viscosity \( \eta_{r0} \)

Coil overlap concentration [g/L] \( C^* \)

Viscosity upturn concentration for HMWSP [g/L] \( C_n \)

Permeability [mD] \( k \)

Porosity \( \phi \)

Pore volume of the porous media [mL] \( P_v \)

Hydrodynamic pore throat radius [\( \mu m \)] \( r_p \)

Effective hydrodynamic pore throat radius [\( \mu m \)] \( r_p' \)

Injection flow rate [mL/h] \( Q \)

Entry section of the core (0-1cm) \( E \)

1\textsuperscript{st} internal section of the core (1-5cm) \( S1 \)

2\textsuperscript{nd} internal section of the core (5-9cm) \( S2 \)

Mobility reduction (on the section \( i - i = E \); \( S1 \) or \( S2 \)) \( R_m (R_m^i) \)

Permeability reduction (on the section \( i - i = E \); \( S1 \) or \( S2 \)) \( R_k (R_k^i) \)

Effluent viscosity [Pa.s] \( \eta \)

Viscosity of the injected solution [Pa.s] \( \eta_0 \)

Relative effluent viscosity \( \eta/\eta_0 \)

Wall shear rate \( \gamma \)

Effective wall shear rate \( \gamma_{eff} \)

Thickness of the adsorbed polymer layer on the pore wall (on the core section \( i - i = E \); \( S1 \) or \( S2 \)) \( \epsilon_h (\epsilon_h^i) \)

DLS Dynamic Light Scattering

HMWSP Hydrophobically Modified Water Soluble Polymer

HPAM Partially Hydrolysed Polyacrylamide

MALS Multi Angle Light Scattering

MSEC Micellar Size Exclusion Chromatography

WSP Water Soluble Polymer

References


How to get the best out of hydrophobically associative polymers for IOR? New experimental insights


