

Evaluation of pH-Sensitive Hydrogels to Control the Permeability Anisotropy of Oil Reservoirs

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ABSTRACT: In stratified or fractured oil reservoirs, the oil recovery efficiency tends to be low as the injected fluid flows mainly through the matrix's most permeable regions, leaving behind part of the displaceable oil in the matrix's unswept zones. Given this issue, this study aims to evaluate the potential of applying seven commercial samples, based on poly(acrylic acid), to control the anisotropic permeability profile of reservoirs. To perform this study, first, continuous and oscillatory shear tests were conducted to characterize the hydrogel's rheological and viscoelastic behavior in various subsurface conditions (salinity, temperature, and/or pH value). Second, polymer dispersion elution tests were performed in a porous medium to evaluate the matrix's permeability reduction after treatment with hydrogels. The seven commercial samples were classified as pseudoplastic fluids at pH values ranging from 1 to 10. Under typical reservoir conditions, PAAr 70 (which has intermediate molar mass and intermediate number of crosslinks) was the only sample to behave as a strong gel ($G'/G'' > 10$). Elution tests confirmed that the PAAr 70 hydrogel gelified inside the consolidated sandstone plugs and reduced the matrix's permeability four-fold. Therefore, samples based on poly(acrylic acid) with high crosslink density proved to be the most promising for controlling the anisotropic permeability profile of heterogeneous oil reservoirs. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40665.

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INTRODUCTION

Oil reservoir rocks are rarely homogeneous porous media, in general presenting variations in the permeability profile along the reservoir's whole length. These heterogeneities arise due to sedimentological, tectonic, and diagenetic processes and influence the fluid flow inside the porous medium, and the hydrocarbons recovery.¹

The oil recovery efficiency and the sweep efficiency in stratified or fractured reservoirs tend to be low even after application of secondary recovery and improved oil recovery methods. This is because the injected fluids tend to flow through the most permeable regions of the porous medium, leaving behind part of the displaceable oil contained in unswept parts of the rocky matrix.^{2,3}

In this way, the modification of stratified or fractured reservoirs' permeability profile, through techniques based on temporary plugging of the high permeability regions, can be advantageous in various aspects: (i) to promote divergence of injected fluids

to areas of low permeability, (ii) to minimize the injected fluid canalization effect through the network of fractures, and (iii) to prevent the premature arrival of injected fluid (breakthrough) to the producing wells.⁴

The plugging of a reservoir's high permeability regions can be done through: (i) formation of an *in situ* gel or (ii) adsorption/swelling of pre-crosslinked hydrogels within the rock pores.⁵

According to Suk Kyoon et al.⁶ and Kazempour and Alvarado,⁷ pH-sensitive polymer suspensions, based on poly(acrylic acid), proved to be promising to control the anisotropic distribution of porous media permeability, by having programmable gelling time, good injection and propagation, as well as stability in reservoir conditions.

However, despite the great importance of developing a method for applying pH-sensitive hydrogels for conformation control of reservoirs, the literature consulted does not provide precise data on the influence of formulation (polymer concentration, molar mass, and number of crosslinks) and subsurface conditions (pH

value, presence of monovalent and/or divalent ions, temperature, and pressure) on the rheological behavior and viscoelasticity of these materials sensitive to pH value.

Thus, this study assesses the potential for application of commercial pH-sensitive gelling systems, based on poly(acrylic acid), to control the anisotropic permeability profile of heterogeneous oil reservoirs. Both the rheological and viscoelastic behavior of hydrogels, pre-crosslinked or not, with different chemical compositions and crosslink density, were evaluated under conditions typically found in oil reservoirs (temperature, salinity, and pH value).

EXPERIMENTAL

Materials

Seven commercial samples based on poly(acrylic acid), pre-crosslinked or not, with different chemical compositions, equivalent molar mass¹ and number of crosslinks, were selected for the study.

The five pre-crosslinked samples, sold under the brands Carbopol[®] and Flogel, manufactured respectively by Noveon (OH) and SNF (GA), were named in this work as PAAr 20, PAAr 40, PAAr 70, PAAr 80, and PAAr 100, based on the identifications of the suppliers.

The two non-crosslinked poly(acrylic acid) samples, with average viscosimetric molar mass of $1.25 \times 10^6 \text{ g mol}^{-1}$ and $4.0 \times 10^6 \text{ g mol}^{-1}$, made by Sigma-Aldrich, were named in this work PAA 1250 and PAA 4000, respectively, based on their molar masses.

The seven samples based on poly(acrylic acid), received in the form of fine white powders, were not purified prior the characterization tests, the study of their rheological behavior and the elution test in porous medium.

Sample Characterization

The seven hydrogels were characterized by means of Fourier Transform Infrared Spectroscopy (FTIR). The FTIR spectra were obtained in a Varian 3100 Excalibur infrared spectrometer, with a resolution of 4 cm^{-1} for 100 scans, over the spectral region of 4000 cm^{-1} to 650 cm^{-1} , at $30 \text{ }^\circ\text{C}$, using a Pike MIRacleTM attenuated total reflectance accessory equipped with zinc selenide crystal. The spectra were obtained directly from the powdered samples.

Evaluation of Hydrogels' Rheological and Viscoelastic Behavior in Typical Reservoir Conditions

The stock hydrogel samples were prepared by slowly dispersing 0.5 % w/w, 1.0 % w/w or 1.5 % w/w of polymer in deionized water or saline—1.0 % w/w of NaCl, 3.0 % w/w of NaCl or 1.0 % w/w of CaCl_2 —at $30 \text{ }^\circ\text{C}$, under moderate magnetic stirring.

The stock samples, with pH value of 3 (for PAA 1250, PAA 4000, PAAr 70, PAAr 80, and PAAr 100 samples) or 4 (for

PAAr 20 and PAAr 40 samples) were kept under constant magnetic stirring at $30 \text{ }^\circ\text{C}$, for 12 h to guarantee complete hydrogel dissolution and, after this time, remained at rest for 6 h to eliminate air bubbles produced during the preparation process.

Before starting the tests, the pH values of four aliquots of each stock-sample were adjusted to 1, 5, 7, and 10 with the aid of an Oakton Ion6 Acorn Series digital pH meter by adding to the formulations 5.0 mol L^{-1} of an aqueous solution of sodium hydroxide (NaOH), leading to pH values above 3 mol L^{-1} or 1.0 mol L^{-1} of an aqueous solution of hydrochloric acid (HCl) to obtain pH values below 3. The pH value adjustment was conducted with concentrated acid or alkaline solution to minimize the dilution effect during the rheological tests.

The hydrogels' rheological properties were measured in a TA Instruments AR-2000 rheometer by putting approximately 1 mL of each sample on a disposable aluminum parallel plate accessory with 25 mm diameter and then adjusting the gap between the plates to $1000 \text{ }\mu\text{m}$.

The influence of selection/formulation process of the gel systems (like polymer concentration and crosslink density) as well as the typical subsurface conditions of an oil reservoir (pH value, monovalent and/or divalent ions, and temperature) on the hydrogels' rheological behavior and viscoelasticity was systematically analyzed by means of steady and oscillatory shear tests conducted in the linear viscoelasticity region⁸ of the crosslinked and non-crosslinked samples, as shown in Table I.

The region of linear viscoelasticity was determined by oscillatory shear test for the seven samples by sweeping the strain in the range of 0.1 % to 400 % at a constant frequency of 1 Hz. In the sequence, new dynamic tests of frequency sweep in the range of 0.1 Hz to 100 Hz were performed for all samples at the selected strain of 1.0 % (which was within the linear viscoelastic region for all the samples).

The tests sought to reproduce the behavior of commercial samples based on poly(acrylic acid) in an oil reservoir at $80 \text{ }^\circ\text{C}$, salinity of $10,000 \text{ mg L}^{-1}$ of monovalent (NaCl) or divalent (CaCl_2) ions and pH value around 7.

The criterion used to evaluate the potential application of hydrogels in reservoirs was selected on the basis of studies conducted by Suk Kyoon et al.,⁶ Wang et al.,⁹ Lalehrokh and Bryant¹⁰ and Vega et al.¹¹

According to these authors, to control the oil reservoir's conformation, hydrogels must: (i) present the highest values of apparent viscosities for pH values between 5 and 9, and (ii) behave as strong gels, i.e., $G'/G'' > 10$, where G' and G'' are independent from frequency oscillation,¹² in subsurface conditions—pH value 7, $80 \text{ }^\circ\text{C}$, and/or the presence of ions.

The commercial samples forming strong gels ($G'/G'' > 10$, with G' and G'' independent of frequency oscillation) in the presence of ions, at $80 \text{ }^\circ\text{C}$ and pH value 7, were used for elution tests in a porous medium.

¹In this work, the molar mass of pre-crosslinked samples is given as equivalent molar mass. This parameter equals the sum of molar mass of the net segments between crosslinks that shape the hydrogel's tridimensional chain.

Table I. Experimental Conditions Used in the Rheological Tests

Test	Objective	Experimental conditions
Oscillatory shear test with strain sweep	Determine stability of samples and provide information about the linear viscoelasticity region	Strain: 0.1 % to 400 % Frequency: 1 Hz Temperature: 30 °C or 80 °C
Oscillatory shear test with frequency sweep	Characterize the conformation and the intermolecular interactions of polymeric systems by providing information about the elastic and viscous behavior of the samples at different frequencies, without causing rupture of polymer chains	Strain: 1.0 % Frequency: 0.1 Hz to 100 Hz Temperature: 30 °C or 80 °C
Steady shear test with shear rate sweep	Determine the apparent viscosity of the samples	Shear rate: 0.1 s ⁻¹ to 400 s ⁻¹ Temperature: 30 °C or 80 °C
Temperature variation test	Evaluate the influence of temperature on samples' rheological properties	Shear rate: 7 s ⁻¹ or 100 s ⁻¹ Temperature: 30 °C to 80 °C

Evaluation of Gelling and Elution of Hydrogels in Rock Plugs

Six steps were used in the experimental tests to determine the permeability reduction factor (PFR) of sandstone plugs treated with polymer dispersions based on poly(acrylic acid):

Step 1: Assembly of test cell containing rock plugs. During Step 1, Botucatu consolidated sandstone plugs were selected—with 3570 mD average permeability and porosity around 32 %—to simulate the elution of hydrogels in reservoir highly permeable layers.

Step 2: Saturation of rock plugs with saline. During Step 2, the plug within the test cell was saturated with an aqueous solution of 1.0 % w/w NaCl.

Step 3: Elution of saline in test cells and determination of pressure differential during the test (determination of k_0).

Step 4: Elution of polymer dispersion in test cells and determination of pressure differential during the test.

Step 5: Rest of polymer dispersion within test cells for a given period for formation of hydrogels within the porous medium.

Step 6: New elution of saline in test cells after treatment with polymer and determination of pressure differential during the test (determination of k_g).

During Steps 3, 4, and 6, 1.5 porous volume (PV) of 1.0 % w/w NaCl solution or of 1.0 % w/w polymer dispersion was eluted over the cells at a constant volumetric flow of 1 mL min⁻¹ and the pressure differential on the rock plug was monitored and registered.

The polymer concentration, volumetric flow, and the rest times used were selected based on Lalehrokh and Bryant¹⁰ and Al-Anazi and Sharma.¹³ The elution tests in the porous medium were performed at 30 °C in duplicate.

The pressure differential during permeation of saline, before, and after the elution of gelled polymer dispersions, was used for the calculation of the PFR of rock plugs, eq. (1). The PFR is a

parameter used by various authors to evaluate the efficiency of the elution and gelling step of polymer dispersions in porous media.^{6,10,14}

$$\text{PFR} = \frac{k_0}{k_g} = \frac{\Delta P_g}{\Delta P_0} \quad (1)$$

where k_0 is the initial effective permeability of the porous medium to fluid elution, k_g is the effective permeability of the porous medium to fluid elution after polymer dispersion elution and hydrogel formation inside the matrix, ΔP_0 is the pressure differential along the rock plug during saline elution (Step 3), ΔP_g is the pressure differential along the rock plug during saline elution (Step 6).

For this, the following assumptions were considered for application of the Darcy's law: (i) at each test step, the injected fluid saturates 100 % of the porous medium, (ii) the flow inside the porous medium is isothermal, laminar, and stationary, (iii) injected fluids are incompressible, homogeneous, and have invariant viscosity with pressure, and (iv) the porous medium is homogeneous and the $\frac{q \cdot \mu \cdot L}{A}$ ratio is constant during Steps 3 and 6 of the test.

PRF values higher than 1 indicate that the polymer gel formed inside the rock matrix is able to reduce the permeability of the porous medium. According to Lalehrokh and Bryant,¹⁰ the higher the PRF value, at subsurface conditions, the bigger the hydrogel application potential is for controlling the permeability anisotropy of oil reservoirs.

RESULTS AND DISCUSSION

FTIR

The comparative Fourier transform infrared spectra of the seven samples based on poly(acrylic acid), recorded in the 4000 cm⁻¹ to 650 cm⁻¹ wavenumber range at 30 °C, are presented in Figure 1.

The spectra of the seven commercial samples, crosslinked or not, showed absorbance peaks characteristic of poly(acrylic acid).^{15–18}

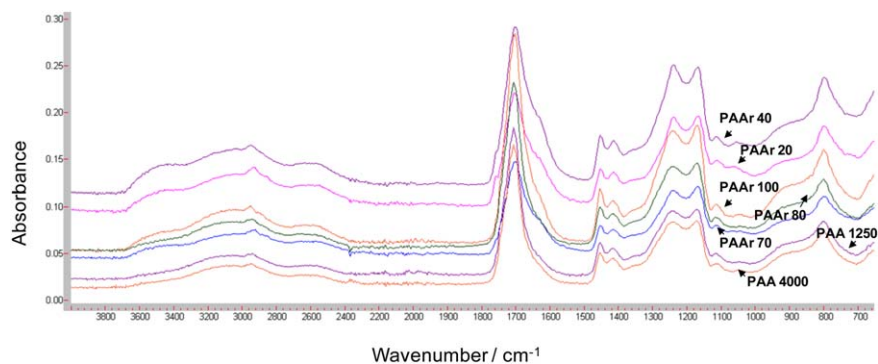


Figure 1. FTIR spectra of samples based on poly(acrylic acid). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

For all samples, the strong intensity band centered at 1710 cm^{-1} is associated with the axial deformation of carbonyl ($\text{C}=\text{O}$) of the non-ionized carboxyl group, which participates in intra- and intermolecular hydrogen bonds ($\text{OH}\cdots\text{O}=\text{C}$).^{17,19}

The characteristic absorptions of the carboxylic ion are: (i) a band of strong intensity between 1650 cm^{-1} and 1550 cm^{-1} related to the asymmetrical axial deformation of the $\text{C}=\text{O}$ bond and (ii) a low intensity band centered at 1400 cm^{-1} , attributed to the symmetric axial deformation of the $\text{C}=\text{O}$ bond.^{15,20}

In the spectra of commercial samples, crosslinked or not, absorption bands placed between 1520 cm^{-1} and 1000 cm^{-1} can be assigned to: (i) angular deformation of the CH_2 group between 1470 cm^{-1} and 1440 cm^{-1} , (ii) angular deformation of the $\text{O}-\text{H}$ bond, between 1440 cm^{-1} and 1390 cm^{-1} , (iii) axial deformation of the $\text{C}-(\text{C}=\text{O})=\text{O}$ group between 1320 cm^{-1} and 1210 cm^{-1} , and (iv) axial deformation of the $\text{C}-\text{O}-\text{C}$ group, between 1200 cm^{-1} and 1130 cm^{-1} .^{17,20}

Furthermore, for the five pre-crosslinked hydrogels, two additional absorption bands are overlapped by axial deformations of the $\text{C}-(\text{C}=\text{O})-\text{O}$ group (between 1320 cm^{-1} and 1210 cm^{-1}) and the $\text{C}-\text{C}-\text{O}$ group (between 1200 cm^{-1} and 1130 cm^{-1}) of poly(acrylic acid): (i) a band between 1250 cm^{-1} and 1200 cm^{-1} , related to the axial deformation of the $\text{C}-\text{O}-\text{C}$ group of ether within the structure of copolymerized acrylates with acrylic acid, and (ii) a band between 1170 cm^{-1} and 1160 cm^{-1} , associated with axial deformation of the $\text{C}-\text{O}-\text{C}$ group of polyfunctional ethers used as crosslinking agents for the samples' synthesis.¹⁷

According to the literature, the crosslinking agents used by manufacturers for the synthesis of the five pre-crosslinked hydrogels evaluated are allyl ethers of polyols.^{15,16,21} These polyfunctional compounds form covalent bonds with chains of poly(acrylic acid) from the unsaturation of allyl groups ($-\text{CH}_2-\text{CH}=\text{CH}_2$) but without significantly altering the profile of the absorption bands of pre-crosslinked hydrogels, when compared with the non-crosslinked samples.

Characteristics of the Hydrogels Based on Poly(acrylic acid)

The commercial samples of pre-crosslinked hydrogels are composed by polymer chains of poly(acrylic acid) of high equivalent

molar mass crosslinked with compounds that provide stability to hydrolysis and high temperatures.^{17,21}

The absorption bands of non-crosslinked PAA 1250 and PAA 4000 samples were used as the basis for qualitative comparisons of the composition and number of crosslinks of the pre-crosslinked samples. For this purpose, two band ratios were calculated based on FTIR spectra of the samples, denominated (acrylate/acid) band ratios, and (crosslinking agent/acid) band ratios, presented in Table II.

The (acrylate/acid) band ratio was determined by dividing the band absorbance peak between 1300 cm^{-1} and 1230 cm^{-1} , associated with the deformation of the $\text{C}-(\text{C}=\text{O})-\text{O}$ group of poly(acrylic acid) and the $\text{C}-\text{O}-\text{C}$ group of acrylate copolymer, by the band absorbance peak between 1440 cm^{-1} and 1390 cm^{-1} , associated with the deformation of the $\text{O}-\text{H}$ bond of carboxylic acid (Figure 1).

The (crosslinking agent/acid) band ratio was determined by dividing the band absorbance peak between 1200 cm^{-1} and 1140 cm^{-1} , attributed to deformation of the $\text{C}-\text{O}-\text{C}$ group of poly(acrylic

Table II. (Acrylate/Acid) and (Crosslinking Agent/Acid) Band Ratios and Qualitative Comparisons Between Samples Based on Poly(acrylic acid)

Samples	Band ratio (acrylate/acid)	Band ratio (crosslinking agent/acid)	% of acrylates	Number of crosslinks
PAA 1250	1.79	1.82 ^a	--	--
PAA 4000	1.88	1.84 ^a	--	--
PAAr 20	2.34	2.31	+++	++++
PAAr 40	2.31	2.26	++	+++++
PAAr 70	2.12	2.15	+	+++
PAAr 80	2.03	2.06	+	++
PAAr 100	1.96	2.00	+	++

(--) not applicable, (+) very low, (++) low, (+++) intermediate, (+++++) high, and (+++++) very high.

^aDespite these samples do not have chemical crosslinks, promoted by the crosslinking agent, the calculation of the band ratio was performed to serve as a reference for qualitative comparisons with the pre-crosslinked commercial samples.

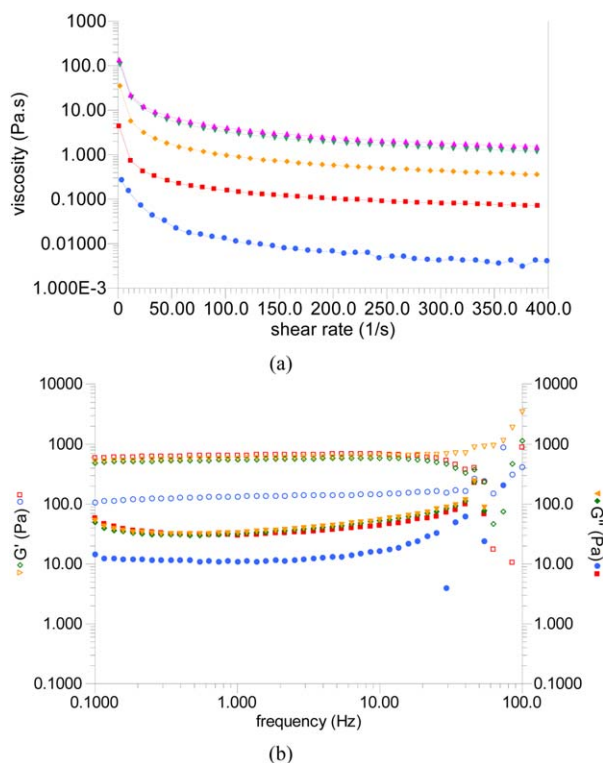


Figure 2. Curves for 1.0 % w/w PAAr 70 samples at 30 °C and different pH values: (a) apparent viscosity curves: ● pH 1, ■ pH 3, ▲ pH 5, ◆ pH 7, and ★ pH 10, and (b) variation of G' and G'' according to the frequency at 1.0 % strain: ○ pH 3, □ pH 5, ◇ pH 7, and ▼ pH 10. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

acid) and the C—O—C group of the crosslinking agent, by the band absorbance peak between 1440 cm^{-1} and 1390 cm^{-1} , associated with the deformation of the O—H bond of carboxylic acid.

The five pre-crosslinked commercial samples have a low total number of crosslinks and low content of acrylate because the values of (crosslinking agent/acid) and (acrylate/acid) band ratios were slightly higher than those for samples of non-crosslinked poly(acrylic acid).²²

In the PAAr 20 sample, the value obtained for (crosslinking agent/acid) band ratio includes the absorption of the crosslinking agent and acrylate bands overlapped by the absorption band characteristic of the C—O—C group (between 1240 cm^{-1} and 1177 cm^{-1}) of polyethylene glycol (PEG). This statement is based on data obtained from the literature for the sample in question.^{23,24}

According to Gomez-Carracedo et al.¹⁶ and Kim et al.,²¹ PAAr 20 and PAAr 40 have high equivalent molar masses and PAAr 20 has fewer number of crosslinks than PAAr 40.

Based on the literature and analysis of the FTIR spectra and (acrylate/acid) and (crosslinking agent/acid) band ratios, relative and qualitative comparisons regarding the composition and the number of crosslinks for the seven commercial samples evaluated were suggested and are presented in Table II.

Evaluation of Hydrogels' Rheological and Viscoelastic Behavior in Reservoir Conditions

The application of steady and oscillatory shear on the seven hydrogel samples was used to measure the flow resistance and the viscoelasticity of the hydrogels, by varying: (i) pH value, (ii) salinity, (iii) temperature, and (iv) polymer concentration.

Although suspensions of hydrogels are biphasic systems, they were considered as pseudo-homogeneous systems for the rheological steady and oscillatory shear studies.⁸

Evaluation of the pH Value's Influence on the Viscoelastic and Rheological Behavior of the Hydrogels

Viscosity curves in function of shear rate and variation of the elastic modulus (G') and viscous modulus (G'') in function of frequency of dispersions based on 1.0 % w/w poly(acrylic acid), at 30 °C, prepared in deionized water with pH values adjusted to 3 (for PAA 1250, PAA 4000, PAAr 70, PAAr 80, and PAAr 100 samples) or 4 (for PAAr 20 and PAAr 40 samples), as well as 5, 7, and 10 were obtained. All samples presented similar rheological behavior and Figure 2 shows the typical curves obtained for PAAr 70 sample.

According to the shape of the apparent viscosity curve, the seven dispersions based on poly(acrylic acid) can be classified as non-Newtonian fluids for all analyzed pH values.

At rest, the polymer dispersions form a structured network, mainly due to entanglement of polymer chains, giving the system resistance to flow.

The reduction in apparent viscosity as the shear rate increases results from the polymer chains' and three-dimensional networks' unfolding and alignment in the flow direction. Such behavior is reversible and the system recovers the initial viscosity when the applied shear is reduced or ceased.

At pH values below 3, the carboxylic acrylic acid (COOH) groups are protonated, keeping the polymer chains folded. Under these conditions, the apparent viscosity of the samples is low, a characteristic that ensures good injection and propagation of polymer dispersions based on poly(acrylic acid) in porous media.⁶

For pH values above 3 (for PAA 1250, PAA 4000, PAAr 70, PAAr 80, and PAAr 100 samples) or 4 (for PAAr 20 and PAAr 40 samples), the acrylic acid carboxylic groups undergo ionization (COO^-), with the occurrence of intra- and intermolecular electrostatic repulsions that promote the unfolding of polymer chains (with absorption of water inside the three-dimensional network) and the increase in apparent viscosity during the distention process of the samples.^{6,25}

Maximum neutralization of acrylic acid carboxylic groups of the commercial samples analyzed occurred at a pH value around 7, the value typically found in oil reservoirs.

The elastic behavior of the samples is assigned to the entanglement of polymer chains, crosslinks and/or intermolecular hydrogen bonds with the solvent. On the other hand, the viscous behavior of hydrogels is mainly due to the polymer chain motion.²¹

Above 1 Hz (for PAA 1250 sample) and 10 Hz (for PAA 4000, PAAr 20, PAAr 40, PAAr 70, PAAr 80, and PAAr 100 samples),

Table III. Elastic Modulus (G') and Viscous Modulus (G'') of Hydrogels Based on Poly(acrylic acid) Prepared in Deionized Water, 1.0 % or 3.0 % w/w NaCl Solution, at 30 °C and pH Value 7, at the Frequency of 1.0 Hz

Samples	G'/G'' (deionized water)	G'/G'' (1.0 % w/w of NaCl)	G'/G'' (3.0 % w/w of NaCl)
PAA 1250	9.92 ± 0.14	8.45 ± 0.12	5.41 ± 0.09
PAA 4000	12.83 ± 0.21	19.44 ± 0.21	13.59 ± 0.16
PAAr 20	24.06 ± 0.71	4.13 ± 0.04	6.65 ± 0.03
PAAr 40	12.27 ± 0.30	10.59 ± 0.15	8.01 ± 0.12
PAAr 70	17.15 ± 0.32	27.61 ± 0.23	16.55 ± 0.13
PAAr 80	15.44 ± 0.25	5.16 ± 0.02	4.89 ± 0.04
PAAr 100	15.88 ± 0.34	20.13 ± 0.27	2.86 ± 0.07

the initial three-dimensional structure of the system is destroyed and the hydrogels present frequency-dependent G' and G'' .

The gelled samples showed more rigid structures and better three-dimensional reorganization when compared with the results obtained for the non-neutralized formulations—pH values below 3 (for PAA 1250, PAA 4000, PAAr 70, PAAr 80, and PAAr 100 samples) and 4 (for PAAr 20 and PAAr 40 samples)—in which the G' and G'' variation occurred earlier due to the frequency.

Table III presents the elastic modulus (G') and viscous modulus (G'') of the hydrogels prepared in deionized water at 30 °C and pH value 7, at the frequency of 1.0 Hz.

According to the results, the samples PAA 4000, PAAr 20, PAAr 40, PAAr 70, PAAr 80, and PAAr 100 presented rheological response characteristic of strong gels, with high perfection of three-dimensional macromolecular networks.²⁶ Also, G' is larger than G'' ($G'/G'' > 10$), and both are independent of frequency variation.

The PAA 1250 sample, on the other hand, is strictly classified as a weak gel, where G' is slightly larger than G'' ($G'/G'' < 10$), with both being slightly dependent on frequency.¹² However, due to the G'/G'' ratio close to 10, the sample was not excluded from the next hydrogel assessment step.

As the seven commercial samples showed high sensitivity to variations of the medium's pH value, with gelling at pH above 5, new hydrogels were prepared in saline to evaluate the influence of salt concentration as well as ionic valence on the viscoelastic and rheological behavior of these materials.

Evaluation of Salinity's Influence on the Viscoelastic and Rheological Behavior of Hydrogels

Typical apparent viscosity curves in function of shear rate and variation of elastic modulus (G') and viscous modulus (G'') in function of frequency, studied in the linear viscoelastic region of the dispersions based on 1.0 % w/w poly(acrylic acid), at 30 °C, prepared in NaCl solution, with pH value set at 3 (for PAA 1250, PAA 4000, PAAr 70, PAAr 80, and PAAr 100 samples) or 4 (for PAAr 20 and PAAr 40 samples) and 7, were obtained. All samples presented similar rheological behavior, and Figure 3 shows the typical curves obtained for PAAr 70 sample.

The experimental results showed that both the salt concentration and ionic valence present in the system affect the apparent

viscosity and the viscous and elastic modulus of the hydrogel dispersions.

The presence of monovalent ions in the medium screens the hydrogel's anionic groups, reducing intermolecular interactions and electrostatic repulsive intramolecular forces of the carboxylic groups. Consequently, the three-dimensional network is kept more folded, and the apparent viscosity and the curves of elastic modulus and viscous modulus in function of frequency are shifted to lower values than those obtained for the samples prepared in deionized water.

The shielding effect on repulsive forces is even more pronounced for samples prepared in 3.0 % w/w solution of NaCl,

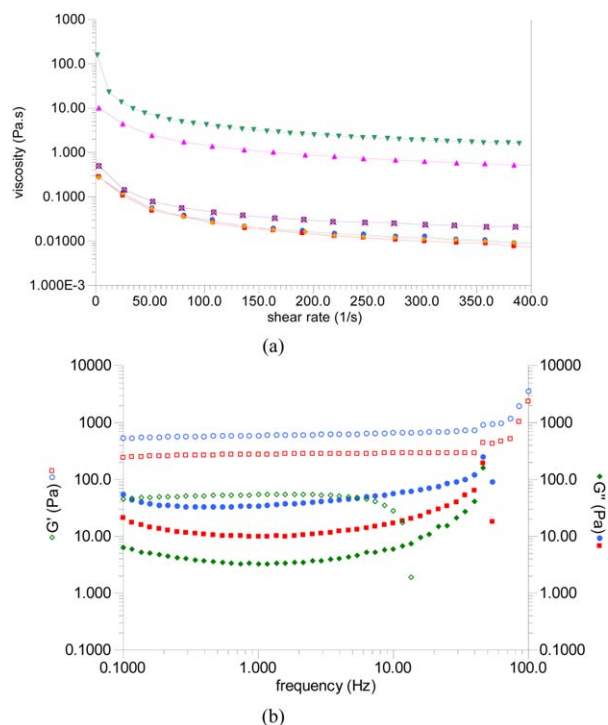


Figure 3. Curves for 1.0 % w/w PAAr 70 samples at 30 °C: (a) apparent viscosity curves for samples prepared in: ■ H₂O pH 3, ■ 1 % NaCl pH 3, ■ 3 % NaCl pH 3, ▲ H₂O pH 7, ▲ 1 % NaCl pH 7 and ■ 3 % NaCl pH 7, and (b) variation of G' and G'' in function of frequency, at 1.0 % strain, for the samples prepared in: ● H₂O pH 7, ■ 1 % NaCl pH 7, and ◆ 3 % NaCl pH 7. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

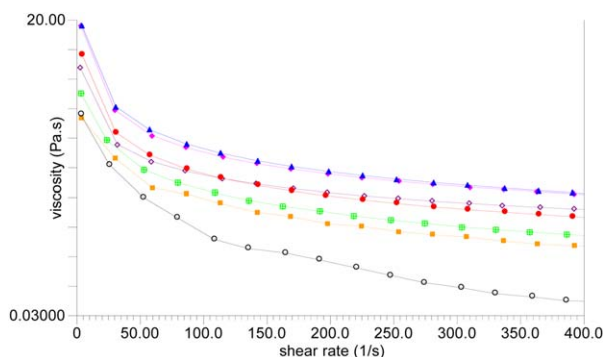


Figure 4. Comparative curves of apparent viscosity for 1.0 % w/w samples prepared in 1.0 % w/w NaCl solution with pH 7, at 30 °C: \blacklozenge PAA 1250, \blacklozenge PAA 4000, \blacksquare PAAr 20, \blacksquare PAAr 40, \blacktriangle PAAr 70, \blacksquare PAAr 80, and \blacklozenge PAAr 100. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

leading to an asymptotic apparent viscosity plateau and even lower elastic and viscous modulus values for all samples.

The seven commercial samples evaluated underwent flocculation in the presence of divalent ions at pH value of 7, preventing performance of the rheological tests. These samples are not recommended for applications in reservoirs whose formation water is naturally hard water.

Figure 4 presents comparative curves of the apparent viscosity of the hydrogels based on poly(acrylic acid) prepared in 1.0 % w/w NaCl solution, at 30 °C and pH value 7.

According to the tests results, the rheological behavior of the hydrogels prepared in a 1.0 % w/w NaCl solution depends on their equivalent molar mass or on the number of crosslinks. The bigger the equivalent molar mass is and/or the smaller the number of crosslinks, the bigger the reduction is of the apparent viscosity of the sample in the presence of ions.

In the non-crosslinked PAA 1250 and PAA 4000 samples, the bigger the molar mass, the bigger the polymer chain folding is. The presence of ions in the formulation weakens the intermolecular electrostatic repulsions of the ionized carboxylic groups and the intermolecular hydrogen bond, sharply reducing the apparent viscosity of the samples with bigger molar mass.

The PAAr 20 and PAAr 40 samples, with bigger equivalent molar mass, underwent greater reduction of apparent viscosity than the pre-crosslinked PAAr 70, PAAr 80, and PAAr 100 samples, with lower equivalent molar mass.

For the PAAr 80 and PAAr 100 hydrogels, with similar number of crosslinks, the smaller apparent viscosity of the PAAr 80 sample can be attributed to the greater influence of ions on the rheological behavior of samples with higher equivalent molar mass.

For pre-crosslinked hydrogels, the bigger the number of crosslinks of the sample, the smaller the mobility and the folding of the three-dimensional network of the hydrogel in the presence of ions. As a consequence, the resulting apparent viscosity tends to be less impacted than in the less crosslinked samples.

The rheological behavior of the PAAr 80 sample, with low number of crosslinks and high equivalent molar mass, was strongly influenced by the presence of monovalent ions in the medium. The greater relative mobility of the hydrogels' three-dimensional network and, as a consequence, the greater folding of the chains in the presence of ions, resulted in smaller apparent viscosity when compared to the PAAr 70 and PAAr 100 hydrogels.

On the other hand, the PAAr 70 sample, with intermediate number of crosslinks and intermediate equivalent molar mass, in the presence of ions, underwent the least viscosity reduction among the seven commercial samples evaluated, behaving rheologically like the non-crosslinked PAA 4000 sample.

Table IV presents relative and qualitative comparisons regarding the equivalent molar masses suggested for the commercial pre-crosslinked samples, considering the rheological properties and the number of crosslinks in the hydrogels' networks (defined in Table II). The crosslink density shown in Table IV is going to be discussed afterward.

Table III shows the G'/G'' ratio of the poly(acrylic acid) hydrogels prepared in 1.0 % or 3.0 % w/w NaCl solution, at 30 °C, with pH 7, at a frequency of 1.0 Hz.

Under the experimental conditions used, the PAA 4000, PAAr 70, and PAAr 100 formulations showed typical behavior of a strong gel—ratio $G'/G'' > 10$ and G' and G'' independent of the frequency variation—in the presence of 1.0 % w/w NaCl.

The PAAr 40 sample, prepared in 1.0 % NaCl solution, has $G'/G'' \approx 10$, showing intermediate behavior between a strong and a weak gel. Therefore, future studies are suggested to evaluate the viscoelastic behavior of new formulations in a saline environment, with polymer concentrations of 2.0 % w/w to 3.0 % w/w, so the G'/G'' ratio reaches higher values and the sample behaves as a typical strong gel.⁶

The PAA 1250, PAAr 20, and PAAr 80 samples, in the presence of 1.0 % w/w of monovalent ions, originated weak gels, in other words, $G'/G'' < 10$ and G' and G'' modulus are dependent on the oscillation frequency. According to Craig et al.,²⁷ in weak gels the polymer chains are more folded and the proportion of molecular segments that do not participate directly in the elastically active polymeric three-dimensional network is bigger.

With the exception of PAA 4000 and PAAr 70, the other formulations prepared in 3.0 % w/w NaCl solution showed G' and G'' slightly dependent on frequency and $G'/G'' < 10$ —typical behavior of weak gels.

The PAA 4000 and PAAr 70 formulations prepared in 3.0 % w/w NaCl solution behaved as strong gels, making them the most promising formulations for the treatment of high-salinity reservoirs.

Because only the PAA 4000, PAAr 70, and PAAr 100 samples formed strong gels in the presence of 1.0 % w/w of NaCl, new formulations based on these three hydrogels were prepared to evaluate the thermal stability and the influence of temperature on the rheological and viscoelastic behavior of these materials.

Table IV. Qualitative and Relative Comparison of the Crosslink Density of the Samples Based on Poly(acrylic acid)

Samples	Number of crosslinks	Equivalent molar mass	Crosslink density
PAAr 20	++++	+++++	0.8
PAAr 40	+++++	+++++	1.0
PAAr 70	+++	++	1.5
PAAr 80	++	+++	0.7
PAAr 100	++	++	1.0

(+) very low, (++) low, (+++) intermediate, (++++) high and (+++++) very high.

Evaluation of Temperature's Influence on the Rheological and Viscoelastic Behavior of Hydrogels

Typical apparent viscosity curves in relation to the temperature and variation of the elastic modulus (G') and viscous modulus (G'') in function of the frequency, taken in the linear viscoelasticity region of poly(acrylic acid) dispersions at 1.0 % w/w, prepared in deionized water, with pH values adjusted to 3 and 7, were obtained. All samples presented similar rheological behavior, and Figure 5 shows the typical curves obtained for PAAr 70 sample.

According to the test results, the PAA 400, PAAr 70, and PAAr 100 samples maintained their apparent viscosity in all the test temperature range, independent of the pH value. Under the conditions evaluated, these hydrogels did not undergo thermal degradation and abrupt changes in the rheological behavior in relation to temperature, in accordance to results obtained by Barry and Meyer^{28,29} and Weber et al.³⁰ for other poly(acrylic acid) based hydrogels.

When the medium's pH value was close to 3, elevating the test temperature to 80 °C shifted elastic modulus (G') and viscous modulus (G'') curves in function of frequency to lower values than those obtained in the tests at 30 °C.

However, when the pH value was close to 7 and the samples were in gel form, the increase of the test temperature from 30 °C to 80 °C did not affect the behavior of the elastic modulus and viscous modulus in function of frequency of the PAAr 70 and PAAr 100 samples.

According to Barry and Meyer^{28,29} and Weber et al.,³⁰ the thermal stability of these materials can be explained by the elasticity and/or the crosslinked structure of the samples. The crosslinks and the molecular entanglements suppress the thermal fluctuation and/or the increase of thermal mobility of the polymer chains in such a way that increasing the temperature has little effect on the apparent viscosity of pre-crosslinked hydrogels.

Furthermore, it is important to mention that at pH 7 most of the free COOH groups should be in the ionized form (COO^-). Then, in this pH value, the variation of temperature do not cause significant change in the sample's rheological behavior. On the other hand, at the pH 3, wherein the carboxyl groups are not dissociated, the hydrogen bonds occur and the temperature increase

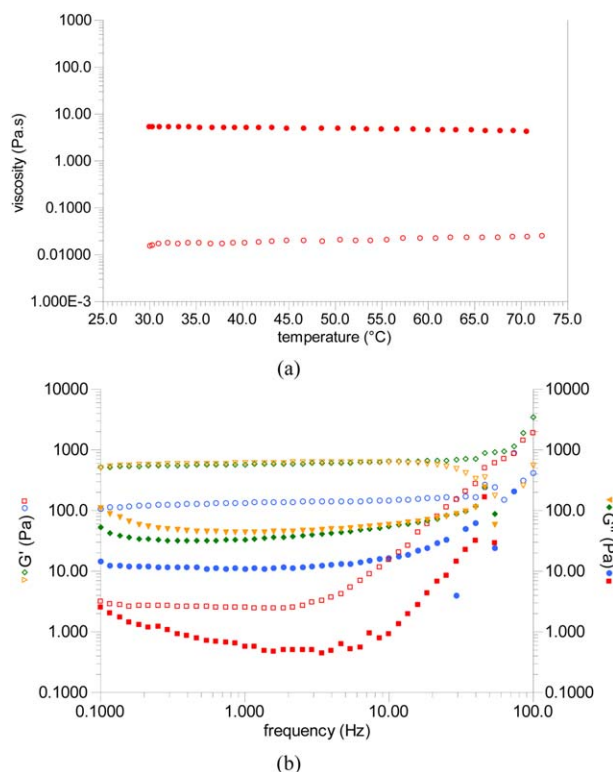


Figure 5. Curves for 1.0 % w/w PAAr 70 samples: (a) apparent viscosity curves in relation to the temperature for samples, with \square pH 3 and \bullet pH 7 values, under 100 s^{-1} steady shear rate, and (b) variation curves of G' and G'' in relation to the frequency, at 1.0 % strain, for samples at: \bullet pH 3 (30 °C), \square pH 3 (80 °C), \diamond pH 7 (30 °C), and \triangle pH 7 (80 °C). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

affects the sample's rheological behavior due to the reduction of the intensity of these interactions.

Table V shows the G'/G'' ratio of the poly(acrylic acid) hydrogels prepared in deionized water, with pH 7, at 1.0 Hz frequency.

At 80 °C, the PAAr 70 and PAAr 100 samples showed behavior typical of a strong gel— $G'/G'' > 10$ and G' and G'' independent of the frequency variation. The PAA 4000 sample, on the other hand, behaved as a weak gel— $G'/G'' < 10$ and G' and G'' dependent on the oscillation frequency. Therefore, it was excluded from the subsequent hydrogel evaluation stages.

New formulations based on PAAr 70 and PAAr 100 were prepared to evaluate the influence of the polymer concentration on the hydrogels' rheological and viscoelastic behavior.

Table V. G'/G'' Ratio of the Poly(acrylic acid) Hydrogels Prepared in Deionized Water, with pH 7, at 30 °C or 80 °C, at Frequency of 1.0 Hz

Samples	G'/G'' at 30 °C	G'/G'' at 80 °C
PAA 4000	12.83 ± 0.11	7.39 ± 0.03
PAAr 70	17.15 ± 0.14	13.72 ± 0.15
PAAr 100	15.88 ± 0.12	13.24 ± 0.11

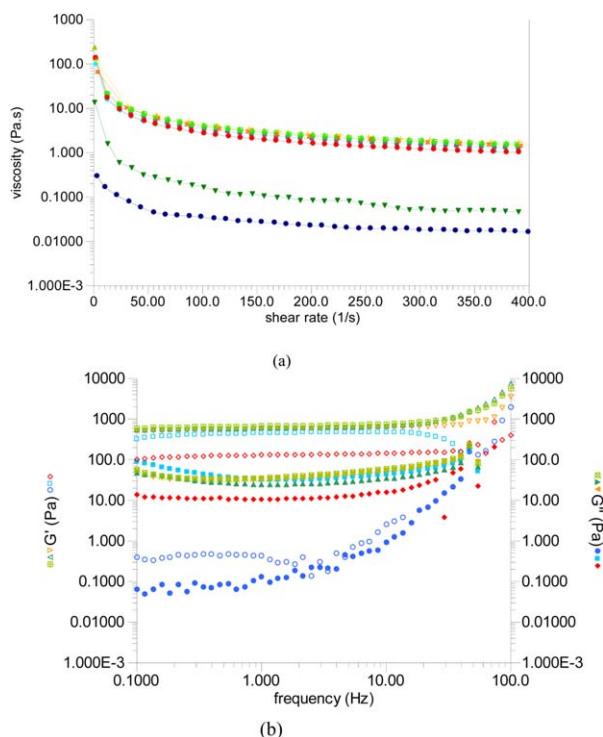


Figure 6. Curves for PAAr 70 samples, at 30 °C, at different polymer concentrations (w/w) and pH values: (a) apparent viscosity curves: ● 0.5 % pH 3, ■ 0.5 % pH 7, ▲ 0.5 % pH 10, ◆ 1.0 % pH 3, ★ 1.0 % pH 7, ▨ 1.0 % pH 10, and ◆ 1.5 % pH 3, ▩ 1.5 % pH 7, and + 1.5 % pH 10, and (b) variation of G' and G'' as a function of frequency, at 1.0 % strain: ○ 0.5 % pH 3, □ 0.5 % pH 7, ◆ 1.0 % pH 3, ▽ 1.0 % pH 7, ▲ 1.5 % pH 3, and ▨ 1.5 % pH 7. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Evaluation of the Influence of Polymer Concentration on the Hydrogels' Rheological and Viscoelastic Behavior

Typical apparent viscosity curves in function of shear rate and variation of elastic modulus (G') and viscous modulus (G'') in function of frequency of the dispersions based on poly(acrylic acid) at 0.5 % w/w, 1.0 % w/w and 1.5 % w/w, at 30 °C, prepared in deionized water with pH values adjusted to 3, 7, and 10, were obtained. All samples presented similar rheological behavior, and Figure 6 shows the typical curves obtained for PAAr 70 sample.

According to the experimental results, as the polymer concentration in dispersion increases in the system, the greater are the intermolecular entanglements, the electrostatic repulsions and the hydrogen bonds between the polymer chains. Consequently, the apparent viscosity and the elastic character (values of G') of hydrogels are greater.^{31,32}

The influence of the polymer concentration on the apparent viscosity curves can be more easily observed at pH values close to 3, when the swelling of the three-dimensional hydrogel networks is not complete. In this condition, the formulations containing 1.5 % w/w of the polymers showed elastic modulus and viscous modulus curves in function of frequency shifted to higher values than those obtained for samples with a polymer concentration of 0.5 % w/w and 1.0 % w/w.

For values of pH close to 7, the condition in which the three-dimensional network is unraveled and the carboxylic groups are dissociated, the increase from 0.5 % w/w to 1.5 % w/w in polymer concentration had little effect on the rheological and viscoelastic behavior—the elastic modulus and the viscous modulus as functions of frequency—as well as the G'/G'' ratio of the samples.

Table VI shows the G'/G'' ratio of the hydrogels prepared in deionized water, with different polymer concentrations, at 30 °C, pH value of 7 and frequency of 1.0 Hz.

The three polymer concentrations showed typical behavior of strong gels ($G'/G'' > 10$ and G' and G'' independent of frequency variation). However, the presence of monovalent ions and the increase in temperature tends to reduce the G'/G'' ratio. Therefore, to evaluate the PAAr 70 and PAAr 100 samples in reservoir conditions, a polymer concentration of 1.0 % w/w was chosen because their rheological and viscoelastic curves were close to those of the formulations containing 1.5 % w/w polymer.

Evaluation of Hydrogels' Rheological and Viscoelastic Behavior in Reservoir Conditions

To evaluate the rheological behavior of hydrogels in reservoir conditions, curves of apparent viscosity were plotted in function of the shear rate of dispersions based on 1.0 % w/w poly(acrylic acid), at 80 °C, prepared in 1.0 % w/w NaCl solution and deionized water, with pH values adjusted to 3 and 7. The results of the rheology tests are presented in Figure 7.

Under the experimental conditions used, the two commercial samples showed a reduction in the apparent viscosity and maintenance of pseudoplastic behavior in the presence of 1.0 % w/w of NaCl, at temperatures around 80 °C and pH of 3 or 7.

As shown in Figure 7, the apparent viscosity reduction was more evident for the formulations using PAAr 100, which is a hydrogel with fewer number of crosslinks in the network and therefore greater molecular mobility. In addition, both commercial samples showed adequate apparent viscosity, around 0.02 Pa s at shear rate of 70 s⁻¹, assuring good injection of these hydrogels in porous medium.

According to Lalehrokh and Bryant¹⁰ and Stalker et al.,³³ at the time of injection on the rocky matrix, formulations based on poly(acrylic acid) should have: (i) pH-value between 1 and 3, to ensure good propagation and to avoid early gelation/buffering of the matrix pores, and (ii) behavior of slightly pseudoplastic fluids, with viscosity values between 0.01 Pa s and 0.02 Pa s and shear rates around 70 s⁻¹.

Table VI. The G'/G'' Ratio of the Samples Based on Poly(acrylic acid) Prepared in Deionized Water, with Different Polymer Concentrations, at 30 °C, pH 7, and Frequency of 1.0 Hz

Samples	G'/G'' (0.5 % w/w of polymer)	G'/G'' (1.0 % w/w of polymer)	G'/G'' (1.5 % w/w of polymer)
PAAr 70	14.11 ± 0.12	17.30 ± 0.13	18.66 ± 0.14
PAAr 100	14.18 ± 0.09	15.88 ± 0.17	16.74 ± 0.13

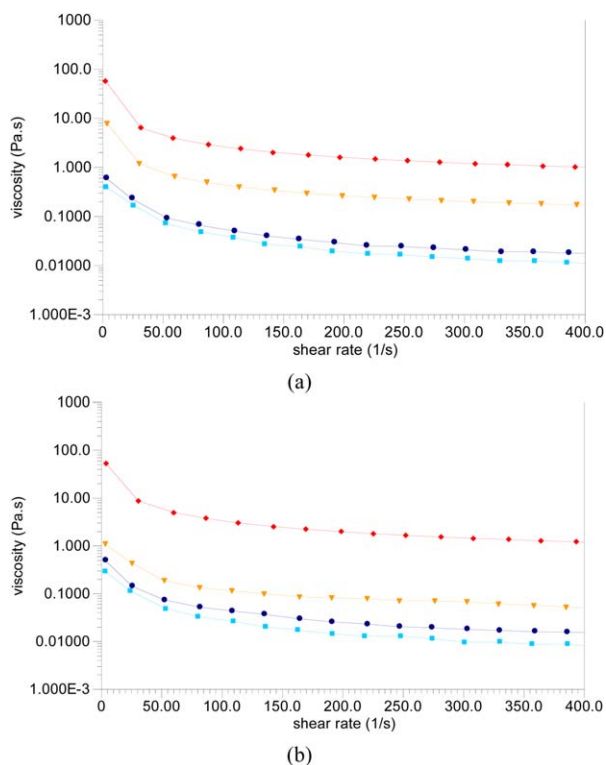


Figure 7. Comparative curves of apparent viscosity at 80 °C for 1.0 % w/w samples prepared in \bullet H₂O pH 3, \blacksquare 1 % NaCl pH 3, \blacklozenge H₂O pH 7, and \blackstar 1 % NaCl pH 7: (a) PAAr 70 sample, and (b) PAAr 100 sample. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The elastic modulus (G') and the viscous modulus (G'') variation curves, as a function of frequency, obtained in the region of linear viscoelasticity of the dispersions based on 1.0 % w/w poly(acrylic acid), at 80 °C, prepared in 1.0 % w/w NaCl solution and deionized water, with pH adjusted to 7, are presented in Figure 8.

As expected, the curves of elastic modulus (G') and viscous modulus (G'') as a function of frequency of the hydrogels prepared in saline solution were shifted to lower values than those obtained in the tests conducted with samples prepared in deionized water.

Under the experimental conditions used, only the formulation based on PAAr 70 behaved as a strong gel ($G'/G'' = 14.85 \pm 0.09$)—elastic component of the response to higher frequency in greater order of magnitude than the viscous component—in the presence of 1.0 % w/w NaCl solution, pH 7 and temperature around 80 °C.

On the other hand, the hydrogel PAAr 100 showed strong gel behavior in the experimental tests in which it was exposed exclusively to one of the variables: (i) presence of 1.0 % w/w NaCl monovalent ions in the formulation or, (ii) elevation of test temperature from 30 °C to 80 °C. However, these variables when associated produced a negative synergistic effect on the behavior of the elastic and viscous moduli curves in function of frequency. When submitted simultaneously to temperatures of 80 °C, in the presence of 1.0 % w/w of monovalent ions and pH values close to 7, the PAAr 100 sample behaved like a weak gel ($G'/G'' = 2.68 \pm 0.02$).

Therefore, from the results obtained from the rheological studies, of the seven commercial samples based on poly(acrylic acid) evaluated, the hydrogel PAAr 70 was selected—with intermediate number of crosslinks and intermediate equivalent molar mass—for experimental elution tests in a porous medium.

The PAAr 70 hydrogel has the highest crosslink density among the commercial samples evaluated. The relative/qualitative crosslink density of the hydrogels—number of crosslinks per equivalent molar mass—was determined using the numerical matching (++) 2, (+++) 3, (++++) 4, and (+++++) 5, as shown in Table IV.

Evaluation of Elution of the Polymer Dispersions in a Porous Medium

To evaluate the efficiency of elution and gelation of the commercial PAAr 70 sample in a plug of consolidated Botucatu sandstone, with average permeability around 3570 mD, the differential pressures through the test cell during the elution of at least 1.5 times the PV of: (i) 1.0 % w/w NaCl solution (Step 3), (ii) polymer dispersion of 1.0 % w/w prepared in 1.0 % w/w NaCl solution (Step 4) and (iii) new 1.0 % w/w NaCl solution (Step 6), were measured and are shown in Figure 9.

The increased differential pressure observed during the elution of the NaCl solution (Step 6) after treatment of the rock plug with the polymer dispersion is attributed to the reduction of

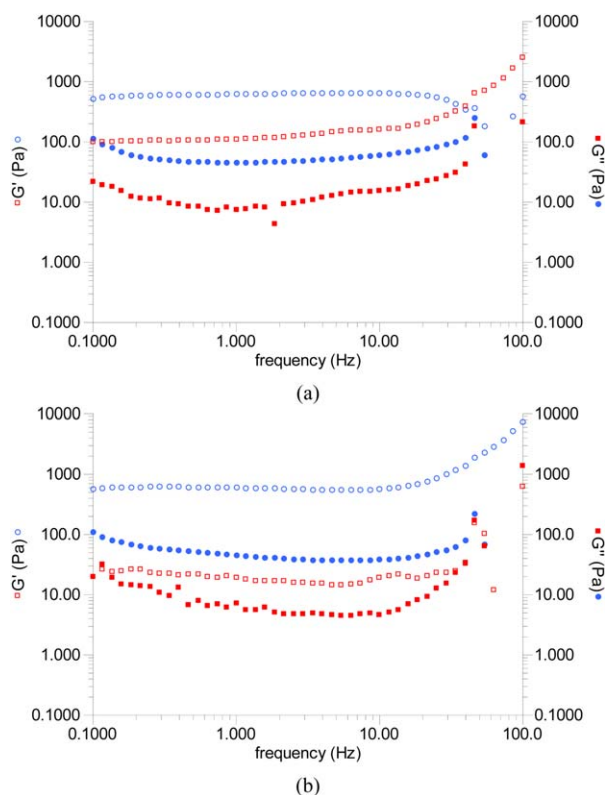


Figure 8. Curves of variation of G' and G'' in function of frequency, at 1.0 % strain, at 80 °C and pH 7, prepared in \circ H₂O and \square 1 % NaCl, for samples of 1.0 % w/w (a) PAAr 70 sample, and (b) PAAr 100 sample. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

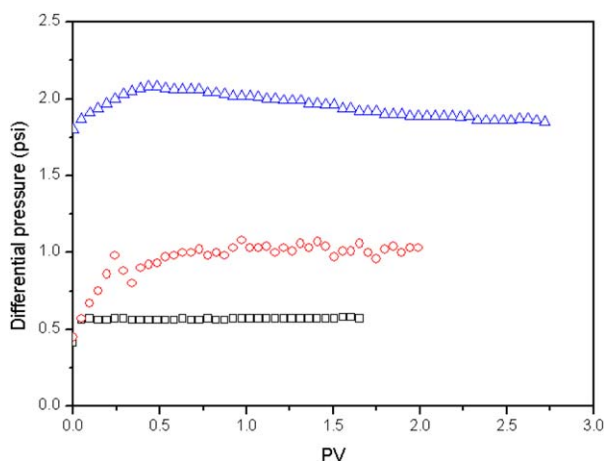


Figure 9. Differential pressure through the test cells, at 30 °C, during the elution of 0.1 mL s⁻¹ of: (a) 1.0 % w/w NaCl solution □ before the elution of the polymer (Step 3) and ▲ 24 h after the elution of the polymer (Step 6), and (b) ○ polymeric dispersion of 1.0 % w/w of PAAr 70 prepared in 1.0 % w/w NaCl solution (Step 4). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the effective permeability of the porous environment due to the gelling of the PAAr 70 sample inside the matrix.

On the other hand, the increase in the differential pressure during the elution of the polymer dispersion (Step 4) is associated with the increased viscosity of the sample as geochemical reactions occur and raise the pH value of the medium. In this step of the test, the sample did not undergo premature gelling.

The average PRF of the Botucatu sandstone plug after elution and gelling of the sample based on poly(acrylic acid) was approximately 4.

According to the results of the elution test, the PAAr 70 sample is promising for controlling the permeability anisotropy of oil reservoirs. This result is in line with those obtained by Choi³⁴ for Carbopol® samples. According to the author, the most appropriate hydrogels for modifying the conformation of reservoirs are those with the highest crosslink density.

CONCLUSIONS

1. Characterization tests (FTIR and rheological tests) provided information on the number of crosslinks, as well as on the differences in the chemical composition of the analyzed samples.
2. The greater relative mobility of the three-dimensional network of pre-crosslinked PAAr 20, PAAr 40, and PAAr 80, hydrogels with high equivalent molar mass, resulted in a larger folding of the chains in the presence of monovalent ions and, consequently, reduced the apparent viscosity and the G'/G'' ratio.
3. The PAAr 100 sample, with relatively low molar mass and relatively low number of crosslinks, began to behave like a weak gel ($G'/G'' < 10$) when submitted simultaneously to a temperature of 80 °C, the presence of monovalent ions and pH value of 7.

4. Of the seven pH-sensitive gelling systems evaluated, only the PAAr 70 sample, with relatively low equivalent molar mass and intermediate number of crosslinks, behaved as a strong gel in typical reservoir conditions—80 °C, 1.0 % w/w NaCl and pH value of 7.
5. The elution test results proved the reduction of permeability of the consolidated sandstone plugs (PRF around 4) after treatment of the matrix with the PAAr 70 polymeric dispersion.
6. Therefore, hydrogels based on poly(acrylic acid) with higher crosslink density are promising to control the permeability anisotropy in heterogeneous oil reservoirs.

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