Rheological Behavior and Scattering Studies of Acrylamide-Based Copolymer Solutions

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Summary: In this paper the chemical structure of an acrylamide-N,N-dihexylacrylamide copolymer was established by IR and NMR. Static and dynamic light scattering in formamide were used in order to evaluate the polymer structural parameters, such as weight-average molecular weight (M_w), second virial coefficient (A_2), radius of gyration (R_G), the form factor P(q) and the hydrodynamic radius (R_H). Additionally to the classical characterization, those results indicated the presence of aggregation, showing that formamide is not a very good solvent, as stated in earlier investigations. The rheological behavior in aqueous solutions was evaluated as a function of the salt concentration. The solutions presented an important viscosity increase in the presence of NaCl and did not show any sensitivity to the presence of CaCl₂. This result is in favor of the oil recovery especially in high salinity reservoirs.

Keywords: amphiphilic polymer; copolymerization; elastic and dynamic light scattering; rheology; viscosity

Introduction

Over the last 20 years, hydrophobically modified water-soluble polymers have found an increasing number of practical applications.[1] Because of their extraordinary viscous properties, they can be used, for example, as thickening agents in paints, cosmetics, for enhanced oil recovery and drag reduction. The polymers are composed of a hydrophilic main chain and a few hydrophobic substituents, which may be randomly attached to the main chain or appended at one or both ends of the chain.^[2] Aggregates, presumably of the micellar type, are formed and act as reversible cross-links between the polymer chains.[1-4] The petroleum recovery applications have focused primarily on polymers with pendant hydrophobes distributed along the backbone that were produced by grafting or copolymerization.^[5]

A meaningful molecular weight determination requires finding a good solvent, in which the polymer is molecularly dispersed and free of any supramolecular aggregates. For hydrophobically modified polyacrylamide some authors have estimated molecular weights from static light scattering experiments using formamide as a solvent. [6-8] In this paper a copolymer of acrylamide and N,N-dihexylacrylamide was synthesized and characterized by static and dynamic light scattering in formamide, in order to evaluate its structural parameters. Rheological measurements in the presence of salt were also taken to highlight the hydrophobic influence on the aqueous polymer solutions.

Experimental Part

Materials

N,N-Dihexylamine, acryloyl chloride and tetrahydrofuran were obtained from Merck. Acrylamide was purchased from Osvaldo Cruz Química. Sodium dodecyl sulphate was obtained from LABSYNTH. Potassium persulphate, calcium chloride



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and sodium chloride were purchased from VETEC. The deuterated solvents, such as chloroform and water, were obtained from SIGMA. All reagents were used as received.

Hydrophobic Monomer Synthesis and Characterization

The *N*,*N*-dihexylacrylamide was prepared by a reaction of acryloyl chloride with the *N*,*N*-dihexylamine, according to the classical procedure. The *N*,*N*-dihexylacrylamide monomer was checked by IR and NMR spectroscopy. The IR spectrum was acquired with an ABB Bomem spectrophotometer and NMR spectra were recorded using a VARIAN Mercury200 spectrometer operating at 200 MHz.

Micellar Copolymerization

The copolymer was prepared by a micellar copolymerization, under a nitrogen atmosphere, using sodium dodecyl sulphate (SDS) as a surfactant and potassium persulphate (K₂S₂O₈) as a free radical initiator. The initial concentration of monomers in water (total of acrylamide and N,Ndihexylacrylamide) was 3% (w/w) and the initiator concentration was 0.3% (w/w) relative to the monomer feed. The surfactant concentration was 3% (w/v) in the feed, based on water volume. The polymerization was carried out at 50 °C for about 1 h. The conditions were chosen so that the number of hydrophobic monomers per micelle (NH) could be calculated by Equation 1:^[10]

$$N_{\rm H} = \frac{[M_{\rm H}]}{([{\rm SDS}] - {\rm CMC})/N_{\rm ag}} \tag{1}$$

where $[M_{\rm H}]$ is the initial molar concentration of hydrophobic monomer, [SDS] is the molar surfactant concentration, CMC its critical micellar concentration and $N_{\rm ag}$ its aggregation number (CMC_{SDS} = 9.2×10^{-3} mol · L⁻¹ and $N_{\rm ag}$ = 60 at the polymerization temperature of 50 °C).^[10]

The copolymer obtained was recovered by precipitation in acetone and washed exhaustively in this solvent to remove all traces of water, surfactant and residual monomers before being dried under reduced pressure.

Copolymer Characterization

a) FTIR Spectroscopy

The FTIR spectrum was acquired with an IV ABB Bomen spectrophotometer by using a KBr disk.

b) Determination of the Hydrophobe Content by NMR

An NMR spectrum was recorded using a VARIAN Mercury200 spectrometer operating at 200 MHz, at 80 $^{\circ}$ C, after dissolution of the sample in D₂O.

c) Static and Dynamic Light Scattering Experiments

Samples preparation: The different concentrations were prepared by weight from individual stock solutions of polymer in formamide. The pure formamide filtered was used to prepare the solutions. The solutions were allowed to stand with magnetic stirring overnight to ensure homogeneity. After reaching the equilibrium all the solutions were filtered through 0.22 μm Teflon filters to eliminate dust or other impurities.

Static light scattering experiment: the elastic and quasi-elastic scattering measurements were performed using the ALV (Germany) apparatus with an automatic goniometer table, a digital rate meter, and a temperature controlled sample cell at 25 ± 0.1 °C. The scattered light of a vertically polarized $\lambda_0 = 6328 \text{ Å}$ was measured at different wavevector $q = (4\pi n_0/$ λ_0)sin($\theta/2$), θ is the scattering angle ranging from 30° to 150° and n_0 is the refractive index of the medium. The ratio KC/I(q), with $K = 4\pi^2 n_S^2 (dn/dc)^2 (I_0 90^\circ / R 90^\circ) / \lambda_0^4 N_{av}$, was measured in steps of 5° of the scattering angle, where n_S is the refractive index of standard (toluene), I_090° and $R90^{\circ}$ are respectively the intensity and the Rayleigh ratio of the standard at $\theta = 90^{\circ}$, (dn/dc) is the increment of refractive index, C the

polymer concentration, and I(q) the intensity scattered by the polymer.

The use of a Zimm-plot [Equations (2)–(4)] allows determination of $M_{\rm w}$, $R_{\rm G}$, A_2 and the form factor P(q). Assuming that the polymer chains are flexible and in a good solvent the overlap concentration can be estimated as: $c^* = M_{\rm w}/(N_{\rm av}4\pi R_{\rm G}^{-3}/3)$, where $N_{\rm av}$ is the Avogadro number. The solutions were prepared at concentrations below c^* , and were allowed to mix for several days. They were then filtered or centrifuged to remove dust or "aggregates" and allowed to equilibrate for a few days prior to measurements.

$$\frac{kC}{I(q)} = \frac{1}{MP(q)} + 2A_2C \tag{2}$$

$$P(q) = \frac{2(e^{-u} + u - 1)}{u^2}; \ u^2 = q^2 R_g^2$$
 (3)

$$\lim P(q)_{q \to 0} \cong 1 - \frac{q^2 R_{\rm g}^2}{3} \tag{4}$$

Dynamic light scattering experiment: the full homodyne autocorrelation functions of the scattered intensity were obtained using the ALV-5000 autocorrelator from ALV, Langen, FRG. The measured intensity-intensity time correlation function is related to the electric field correlation function by Siegert relation:^[11]

$$g^{(2)}(t) = 1 + \beta(|g^{(1)}(t)|^2)$$
 (5)

where β is spatial coherence factor depending upon the geometry of the detection and the ratio of the intensity scattered by polymer to that scattered by the solvent. Generally, $g^{(1)}(t)$ may be expressed by a continuous distribution of decays:

$$g^{(1)}(t) = \int A(\Gamma) \exp(-(\Gamma t) d\Gamma$$
 (6)

where $g^{(1)}(t)$ is the Laplace transform of the decay rate distribution function $A(\Gamma)$. $A(\Gamma)$ gives the relative intensity of light scattered with decay constant Γ and is a function of the number and size of the scatters. The constrained regularization method (CONTIN) developed by Provencher^[12] or similar ones^[13] are now routinely used to analyze the DLS data for polymeric systems

and allow the determination of the distribution A(t) of decay times of the relaxation modes which characterize the ongoing dynamics.

For a dilute solution of spherical, monodisperse particles undergoing Brownian diffusion $g^{(1)}(t)$ may be represented by:

$$g^{(1)}(t) \cong \exp(-q^2 Dt) \tag{7}$$

where *D* is the translational diffusion coefficient.

The diffusion coefficients were calculated from $D=(\Gamma/q^2)_{q\to 0}$ and the equivalent hydrodynamic Radii $R_{\rm H}$ were deduced using Stockes-Einstein relation $D=k_{\rm B}T/f$. $k_{\rm B}T$ is the Botlzman energy and $f=6\pi\eta_0R_{\rm H}$ is the friction coefficient and η_0 the solvent viscosity.

d) Viscometric Study in Dilute Solution

The intrinsic viscosity $[\eta]$, the Huggins coefficient k' and the Kraemer coefficient k''' of the copolymer were determined in distilled water at 25 ± 0.01 °C. Measurements were carried out using an automatic capillary viscometer AVS-360 from Schott-Geräte (Ubbelohde type).

e) Rheological Measurements

Three experiments for the copolymer in sodium chloride aqueous solutions were done. In the first one, the purified polymer was added to sodium chloride solutions with concentrations of 20–100 g \cdot L⁻¹, and the polymer concentration was fixed at $0.5 \text{ g} \cdot \text{L}^{-1}$. In the second case, the reactional medium was diluted until reaching a polymer concentration of 4 g \cdot L⁻¹ and, then, the necessary mass of sodium chloride was added to obtain solutions with concentrations of 20-100 g · L⁻¹ of sodium chloride. In the third case, the reactional medium was diluted with NaCl solutions, so that the final concentrations of this salt were of 20–180 g \cdot L⁻¹, and the polymer concentration was maintained at 4 g \cdot L⁻¹.

The copolymer behavior in calcium chloride was also analyzed. The reactional medium was diluted with calcium chloride solutions so that the polymer concentration was 4 g \cdot L⁻¹ and the CaCl₂ concentration varied from 0.2 to 1 g \cdot L⁻¹.

All the solutions were analyzed at the shear rates of 2, 4, 7, 16 and $46 \, \text{s}^{-1}$, at 55 °C, using a coaxial cylinder sensor DG41, in a RS 150 Haake RheoStress Rheometer.

Results and Discussion

Hydrophobic Monomer Synthesis and Characterization

The hydrophobic monomer N,N-dihexylacrylamide was obtained according to the classical method. [9] A difficulty in the associative polymers preparation is to obtain polymers with both high thickening properties and good water solubility. Generally, these polymers contain only a low amount of hydrophobe to maintain the solubility in water. When the length of the hydrophobic chain increases, the solubility of the copolymer in water decreases, therefore, the range of hydrophobic modification is even more limited. A short alkyl chain allows a higher incorporation, but the resulting polymer provides weak associative properties.^[14] Volpert et al.^[8] showed that this could be attained using twice branched comonomers such dihexylacrylamide.

The structure of N,N-dihexylacrylamide was determined by means of dimensional NMR spectroscopy experiments (¹H and ¹³C spectra) and IR. Protons and carbons were indexed starting from the carbonile function. The geminal protons on the olefinic carbon are denoted a or b, depending on whether they are in cis or trans, respectively. The ¹H NMR spectrum showed peaks at 0.81-0.87 ppm $(t, 3H, H_9)$, 1.24–1.25 ppm (m, 6H, H₈, H₇, H₆), 1.49– $1.52 \text{ ppm } (m, 2H, H_5), 3.15-3.36 \text{ ppm } (m, 2H, H_5), 3.1$ H₄), 5.58–5.64 ppm (dd, 1H, H_{3a}), 6.24– 6.34 ppm (dd, 1H, H_{3b}) and 6.44-6.58 ppm (dd, 1H, H₂). The ¹³C NMR spectrum of N,N-dihexylacrylamide confirmed the structure. It showed peaks at 14 ppm (1C, C_9), at 22-32 ppm (4C, C₈, C₇, C₆, C₅), at 46-54 ppm (1C, C₄), at 126–128 ppm (2C, C₂, C_3) and at 166 ppm (1C, C_1 , corresponding to the carbonile from the dihexylacrylamide). The FTIR spectrum showed a band at 1 648 cm⁻¹ (υ C=O from tertiary amide). The spectrum also showed peaks at 2 958 cm⁻¹, 2 930 cm⁻¹ and 2 859 cm⁻¹ (υ C-H), at 1 609 cm⁻¹ (υ C=C), 1 465 cm⁻¹, 1 430 cm⁻¹ and 1 378 cm⁻¹ (δ C-H) and at 1 193 cm⁻¹ (υ C-N from amide).

Synthesis and Characterization of the Copolymer

The copolymer was obtained by micellar copolymerization of acrylamide with dihexylacrylamide. The $N_{\rm H}$ value for the synthesized copolymer was 2.6. This value informs the length of the hydrophobic sequences along the polymer chain. Candau et al. [15] observed that a acrylamide/N-(4-ethylphenyl)acrylamide copolymer with $N_{\rm H}=2.6$ has a very poor thickening ability. However, N,N-dihexylacrylamide was capable of increasing the sample's viscous power with low values of $N_{\rm H}$.

a) FTIR Spectroscopy

The FTIR spectrum of the copolymer showed a broad band at 3 340 cm⁻¹ (v OH) that could be a result of the humidity presence in the copolymer, overlapping the NH band in this area. The spectrum also showed bands at 2 929 cm⁻¹ (v CH₂ and v CH₃), 2 862 cm⁻¹ (v CH), 1 671 cm⁻¹ (v C=O), 1 602 cm⁻¹ (twisting vibration of NH₂), 1 451 cm⁻¹ and 1 314 cm⁻¹ (v CH₂ and CH₃). However, the presence of hydrophobic groups along the polymer chain couldn't be confirmed by the FTIR spectroscopy, because they are at a low percentage rate and its characteristic bands are overlapped by the acrylamide bands.

b) Hydrophobe Content by NMR

The extremely low amount of hydrophobic comonomer leads to difficulties to assure its incorporation level in the polymer, especially for those consisting of an alkyl chain. Therefore, many authors assumed that this level was equivalent to the initial feed composition. [14] In our case, the hydrophobe incorporation was measured by ¹H NMR from the integration of the corresponding

peaks to the terminal methyl group of the alkyl chain (0.8 ppm) and the CH group in the polymer backbone (2.1 ppm), $^{[8]}$ using the relation HI% = $100(I_{\text{CH}3}/6I_{\text{CH}})$. The copolymer composition was estimated to be 4.0 mol-% of hydrophobic monomer.

c) Static and Dynamic Light Scattering Experiments

The molecular weight of a polymer is an important parameter to be considered when we are studying its viscous properties. Static and dynamic light scattering experiments^[16] allow the determination of the weight-average molecular weight (M_w) , second virial coefficient (A_2) , radius of gyration (R_G) and molecular conformation or the form factor P(q) in dilute solution and diffusion coefficients (or hydrodynamic radius, $R_H^{[17]}$).

The Zimm plot obtained from the acrylamide-N,N-dihexylacrylcopolymer amide is shown in Figure 1. We have not used the small angles data due to the presence of dust in spite of careful and successive filtrations. The $M_{\rm w}$ value, $2.6 \times 10^6 \text{ g} \cdot \text{mol}^{-1}$, is in agreement with the values found in the literature for polymers synthesized by micellar copolymerization, [10] and is probably overestimated (existence of two relaxation modessee the discussion on the DLS results). The A_2 value, 4.166×10^{-5} mol · cm³ · g⁻², shows that the formamide, in the conditions used during the analysis, is not a very good solvent and is rather approaching a theta solvent $(A_2 = 0)$. For flexible polymer chains in good solvent, the A_2 value is around $5 \times 10^{-4} \, \text{mol} \cdot \text{cm}^3 \cdot \text{g}^{-2[18]}$ and, as the solvent quality decreases, its value also decreases. The R_G value measured, 126.1 nm, is higher than that found in the literature for flexible polymers of M_W around 10^6 in a good solvent. [18]

From the SLS, we could also extract the form factor P(q) [Equation (3)] identified as the scattering intensity I(q) = P(q) at infinitely dilute solution $(C \rightarrow 0)$ and a scattering angle = 0. The results shown in Figure 2 giving reasonable agreement with rather a polydisperse coil with $M_{\rm w}/M_{\rm n}=2$.

Typical intensity autocorrelation functions as revealed by DLS on poly(acrylamide-N,N-dihexylacrylamide) at 2 g · L $^{-1}$ for three different angles are displayed on Figure 3. It is clear from the distribution of residuals (not shown), that a monoexponential fit is not satisfactory. Because of this unsatisfactory monoexponential fit, the data were analyzed using double-exponential fits and CONTIN method. From the deduced relaxation time (τ), we have calculated the diffusion coefficient (D) that was converted to the hydrodynamic radius (R_H). Similar behavior was observed in the range of concentration from 0.5 to 5 g · L $^{-1}$.

The DLS measurements [Figure 4(a) at $0.75~g\cdot L^{-1}$ and 4(b) at $5~g\cdot L^{-1}$] showed indeed a bimodal distribution of the

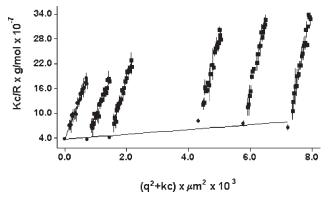


Figure 1. Zimm plot from the copolymer acrylamide-N,N-dihexylacrylamide.

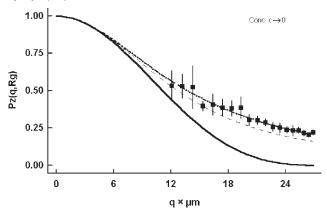


Figure 2. The form factor for a monodisperse coil with $R_G = 126.1$ nm (---), a polydisperse coil with $R_G = 126.1$ nm and polydispersity = 2 (-•-), and a hard sphere with $R_G = 162.79$ nm (—).

relaxation times for the poly(acrylamide-N,N-dihexylacrylamide) in formamide. This suggests that the solutions of this polymer contain structures of two distinct sizes. The relative intensity of the fast mode, corresponding to single chain ($R_{\rm H}=70$ nm), decreases with increasing of the concentration. At the same time the relative of the slow mode ($R_{\rm H}=800$ nm) increases with concentration. At 0.75 g · L⁻¹ 70% of the signal corresponds to single chains and 30% to aggregates. At higher studied concentration, e.g., 5 g · L⁻¹, about 70% of the signal comes from the aggregates. This means that

the copolymer showed a tendency to both intra- and intermolecular association and that the intermolecular association becomes more and more prevailing with increasing the concentration.

d) Viscometric Study in Dilute Solution The intrinsic viscosity $[\eta]$ of a polymer in solution is intimately related to its hydrodynamic volume. The Huggins coefficient (k') is an important measure of the polymer-polymer and polymer-solvent interactions and larger values of 0.5–1 are typically found in poor solvents. Another measure of

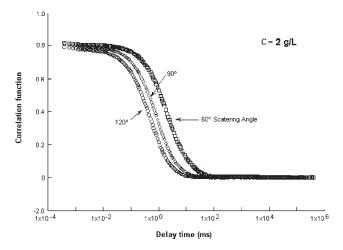


Figure 3.

Autocorrelation function vs time at the scattering angles and concentration indicated.

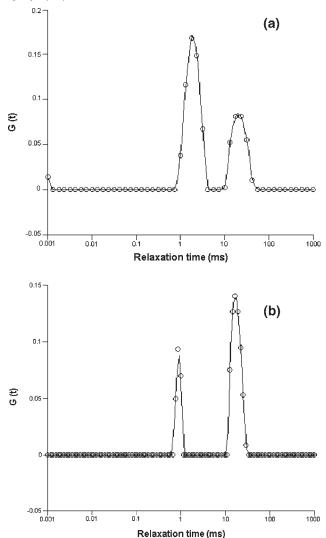


Figure 4. DLS relaxation time distributions in formamide for the copolymer (a) 0.75 g \cdot L⁻¹ and (b) 5 g \cdot L⁻¹.

the solvent quality is the Kraemer coefficient (k''). For polymers in a good solvent its value is negative in sign and smaller in magnitude than k', and k' - k'' = 0.5.^[19]

High values of k' and low of $[\eta]$ reflect the contraction of the polymer chain, due to intramolecular association. Data published in the literature show that these interactions are stronger in copolymers with block structure. When the hydrophobic groups are distributed as discrete units, the copolymers behave as homopolyacrylamides and the k' values are close to those found for polymers in a good solvent (0.4–0.5).^[7] $[\eta]$, k' and k'' of the synthesized copolymer are 414 mL \cdot g⁻¹, 0.59 and 0.05, respectively.

e) Rheological Behavior

Figure 5–7 show how the apparent viscosity of the aqueous copolymer solutions varies with the NaCl concentration, for several shear rates. In the first case (Figure 5), the polymer powder was added to the NaCl solutions so that its final concentration was $0.5\,$ g \cdot L^{-1} and the saline concentrations

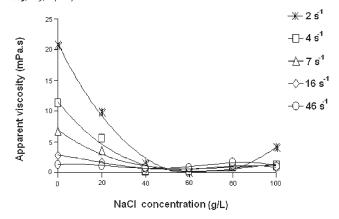


Figure 5. Variation of the apparent viscosity as a function of NaCl concentration, at different shear rates, to the copolymer dissolved in NaCl solutions, at 55 $^{\circ}$ C.

varied from zero to $100~{\rm g}\cdot {\rm L}^{-1}$. The polymer concentration equal to $0.5~{\rm g}\cdot {\rm L}^{-1}$ was used for this analysis because the viscosity of this solution, at $7~{\rm s}^{-1}$ and in the absence of NaCl, presented a value of $6.7~{\rm mPas}$, close to that observed for the petroleum in some reservoirs. [20] As the salt concentration increased, the viscosity decreased.

The reduction of viscosity in Figure 5 can be attributed to the decrease of the solvent quality with the increase of NaCl concentration, which leads to the increase of the hydrophobic interactions, hindering the

complete polymer solubility. These polymer molecules can not distend their chains and the intramolecular associations prevail, reducing the hydrodynamic volume and, consequently, the viscosity.

The following tests (Figure 6 and 7) were made using the crude product. In the Figure 6, the reactional medium was diluted until the polymer concentration of 4 g \cdot L⁻¹ was reached and, then, the salt was added, so that its concentration varied from 0 to $100 \text{ g} \cdot \text{L}^{-1}$. The dilutions of the reactional medium were also made so that its viscosity, in the absence of NaCl, was close to the

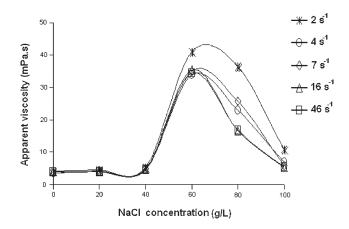


Figure 6. Variation of the apparent viscosity as a function of NaCl concentration, at different shear rates, to the NaCl dissolved in copolymer solutions, at 55 °C.

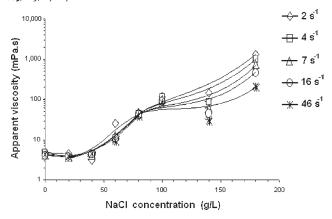


Figure 7.Variation of the apparent viscosity as a function of NaCl concentration, at different shear rates, to mixtures between copolymer solutions and salt solutions, at 55 °C.

viscosity observed for the petroleum in some reservoirs, as commented above. Probably, the reactional medium presents a smaller viscosity, in relation to the purified polymer solution of the same concentration, due to the presence of sodium dodecyl sulfate. The surfactant can interact with the hydrophobic groups, involving them in micelles and reducing the interaction among hydrophobic groups of different chains.[15] The viscosity reached a maximum value around $60 \text{ g} \cdot \text{L}^{-1}$ of salt and later it decreased (Figure 6). This probably happens because intermolecular hydrophobic interactions are established as NaCl is added to the solution, leading to an increase in the viscosity. However, above $60 \text{ g} \cdot \text{L}^{-1}$ of NaCl, it is no longer possible to dissolve this salt in the polymer solution, and the reactional medium acquires an opaque aspect, with phase separation.

In the last case (Figure 7), the crude reactional medium was diluted with NaCl solutions of different concentrations, so that the final polymer concentration was 4 g \cdot L⁻¹ and the final salt concentration varied, initially, from zero to 100 g \cdot L⁻¹. As it was verified that the viscosity increased in the whole analyzed interval, it was decided to increase the saline concentration up to 180 g \cdot L⁻¹, by the dilution of reactional medium with a NaCl solution with a concentration of

 $300~g\cdot L^{-1}$. This concentration was chosen considering that it is the highest salt concentration mentioned in a process of improved oil recovery by polymer flooding.^[21]

The surprising increase of viscosity in Figure 7 can be attributed to the great easiness of interaction between the polymer chains and the salt, when both are dissolved previously in the solution. This type of interaction can lead to the formation of a three-dimensional network of intermolecular connections due to hydrophobic interactions. Up to a concentration of $180\,\mathrm{g}\cdot\mathrm{L}^{-1}$ of NaCl, the formation of two phases was not observed, as happened in the case of salt addition in the solution. However, the material presented an opaque aspect, like an emulsion.

Figure 5–7 showed the influence of the mode as the copolymer has contact with the salt on the rheological properties of the solution. When the salt is added to the polymer solution, the solution viscosity reaches a maximum around $60 \text{ g} \cdot \text{L}^{-1}$ of NaCl, and later it decreases. However, when both, polymer and salt, are already dissolved, the viscosity increase is of the order of hundreds, this can be attributed to the better homogenous mixture. This fact is of great importance when the application in oil wells is sought, because the oil reservoirs have, in general, high salinity. Therefore,

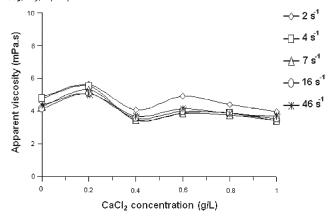


Figure 8. Variation of the apparent viscosity as a function of $CaCl_2$ concentration, at different shear rates, to mixtures between copolymer solutions and salt solutions, at 55 $^{\circ}$ C.

the copolymer could be synthesized in the field and, afterwards, be diluted for the wanted viscosity with the rock formation water.

The polymer behavior in the presence of calcium chloride was also analyzed. All solutions were obtained as described previously. However, the salt concentration was just varied up to $1 \text{ g} \cdot \text{L}^{-1}$, because the Ca^{+2} has a much superior screening power than the Na⁺¹. In Figure 8, it can be observed that the copolymer practically did not have its viscosity influenced by the CaCl_2 presence, until a saline concentration of $1 \text{ g} \cdot \text{L}^{-1}$, at $55 \,^{\circ}\text{C}$.

Conclusion

The characterization of the hydrophobic monomer and the copolymer by NMR and IR confirmed their structures. The static and dynamic light scattering experiments showed that formamide is not a very good solvent for structural characterization of the amphiphilic polymer synthesized, as described in the literature, due to the existence of aggregates clearly highlighted by the elastic and quasi-elastic scattering technique.

In spite of the low concentration of hydrophobic monomer (4 mol-%) the

copolymer presented an odd behavior. The presence of NaCl in the amphiphilic polymer aqueous solutions increased the viscosity at higher polymer concentrations. On the other hand, the amphiphilic polymer solution was tolerant to the Ca+2 presence. Probably, this behavior is related to the formation of hydrophobic interactions, reducing their exposure to water, which leads to the creation of a transitory three-dimensional net. So, the amphiphilic copolymer studied in this work could be used with success in wells with high salinity and hardness. In these cases, the contact of the amphiphilic polymer solution injected into the well with the brine would give rise to a viscosity increase of the medium that could contribute to improved reservoir sweep efficiency, depending on the general conditions of the reservoir and the injection pattern selected.

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