

Solution properties of poly(acrylamide-co-3,5,5-trimethylhexane methacrylate) and its polyelectrolyte derivative

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Abstract The physicochemical properties of hydrophobically modified polyacrylamide (HAPAM) containing a small amount of hydrophobic groups (3,5,5-trimethylhexane methacrylate) and its partially hydrolyzed derivative (HAPAM-10N500) were investigated. The ^{13}C spectrum was used to establish the degree of hydrolysis of HAPAM-10N500. Small-angle X-ray scattering (SAXS) was employed to highlight the polyelectrolyte character of HAPAM-10N500, estimate the chain conformation in the semidilute regime, and evaluate the influence of the ionic strength and the type of salt. The weight average molecular weight, the second virial coefficient, and radius of gyration were determined by static light scattering (SLS). The polymers showed different rheological properties in aqueous solution, with significant increase in viscosity due to partial hydrolysis of HAPAM, however, with strong dependence on ionic strength of the medium. Results showed that the polymers HAPAM and HAPAM-10N500 are suitable for application in processes of moderate temperatures and salinities.

Keywords Hydrophobically modified polyacrylamide · Polyelectrolyte · SAXS · SLS · Rheology

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Introduction

Some water-soluble polymers are characterized by their thickening properties in aqueous media [1, 2]. However, these polymers can exhibit lower viscosity when subjected to mechanical deformations at high shear rates, high temperatures, or increasing ionic strengths [3]. Their rheological properties in aqueous solution can be influenced for both internal factors, such as polymer backbone structure, weight average molecular weight, structure of hydrophobic groups, degree of hydrophobic substitution, degree of hydrolysis, and external factors, such as ionic strength of the medium, pH of the solution, shear rate, temperature, salinity, polymer concentration, and surfactant [1, 4, 5]. These polymers have received an increasing attention due to their viscosifying abilities and rheological behavior, which favor several application possibilities, such as flocculants, in drilling fluids, in hydraulic fracturing, and coatings and thickening agents in oil recovery [6–9], where the control of fluid rheology is required.

Hydrophobically modified polyacrylamide (associative polyacrylamide) consists of an acrylamide backbone containing a low mole percentage of hydrophobic groups, usually in the form of pendant side chains or terminal groups. Hydrophobic groups are typically aliphatic or a mixture of aliphatic and aromatic groups. In aqueous solution, the hydrophobic groups have the tendency to associate through intramolecular and/or intermolecular interactions. Moreover, the increase of ionic strength can lead to an improved viscosity, because the polarity of the medium can strengthen the hydrophobic interactions [10, 11]. Feng et al. studied polyacrylamide (PAM) and hydrophobically modified derivatives with octyl and dodecyl side chains at different hydrophobe lengths and degree of hydrophobic substitution. They showed that the solubility of these polymers with different hydrophobe lengths is different. The associative polyacrylamide with 0.50 or 0.75 mol% of hydrophobe was only soluble for less than 12

carbons in the aliphatic group. In their experiments, they mainly focus on the associative polyacrylamide (H00C8-1.0) containing eight carbons and 1.0-mol% octyl alkyl group. The apparent viscosity of H00C8-1.0, in the semidilute regime (5 g/L) at 25 °C, increased in the presence of the 0.1-mol/L NaCl aqueous solution compared to that in pure water and becomes much higher than that of PAM. This behavior was attributed to the enhancement of intermolecular hydrophobic associations. Moreover, they observed that reduced viscosity of H00C8-1.0 increased with increasing ionic strength of the medium, independent of the nature of the ionic species [10].

On the other hand, solution properties of hydrophobically modified polyelectrolytes differ considerably from those of uncharged associative polymers due to the presence of ionic units within the copolymer [4, 9, 12]. These charged units improve water solubility due to the balance between hydrophobic and electrostatic interactions. McCormick, Middleton, and Cummins reported the synthesis and characterization of hydrophobically modified polyelectrolytes. These polymers were prepared by a micellar technique using acrylamide, *n*-decylacrylamide, and a third monomer, sodium 3-acrylamide-3-methylbutanoate, sodium acrylate, or sodium 2-acrylamide-2-methylpropanesulfonate. The incorporation of *n*-decylacrylamide cannot be determined by conventional methods such as elemental analysis or nuclear magnetic resonance (NMR). These terpolymers exhibit rheological behavior dependent upon the polymer composition, nature of the charged monomer, ionic strength, and pH. Hydrophobic associations in terpolymers with the carboxylate group are stronger than those in structurally analogous terpolymers containing the sulfonate anion, especially at high NaCl concentration [7, 13, 14].

Few reports to date have investigated the hydrodynamic properties of hydrophobically modified polyacrylamides and their partially hydrolyzed derivatives with high degree of hydrolysis using salt solution with different ionic strengths [15]. To the best of our knowledge, the understanding of these properties is a key issue in the literature, because polyelectrolytes with moderate degree of hydrolysis can continue to undergo hydrolysis of amide groups into the warmer petroleum reservoirs. In these systems, which exhibit elevated temperature and higher salt concentration, the properties of the polymeric solutions might be affected, and this fact sometimes becomes a problem in deep reservoirs. So, the goal of this work was to evaluate critically the effect of salinity on the properties of an associative polyacrylamide containing low content of hydrophobic alkyl chain (C9) and its polyelectrolyte derivative with high degree of hydrolysis. The influence of internal (i.e., chemical structure) and external factors (such as polymer concentration, ionic strength, and temperature) on polymer solution properties is a critical point to the development of new suitable polymers for application in enhanced oil recovery processes [16].

In the present study, the physicochemical properties of poly(acrylamide-*co*-3,5,5 trimethylhexane methacrylate) and its partially hydrolyzed derivative were evaluated by small-angle X-ray scattering (SAXS), static light scattering (SLS), and rheology.

Experimental

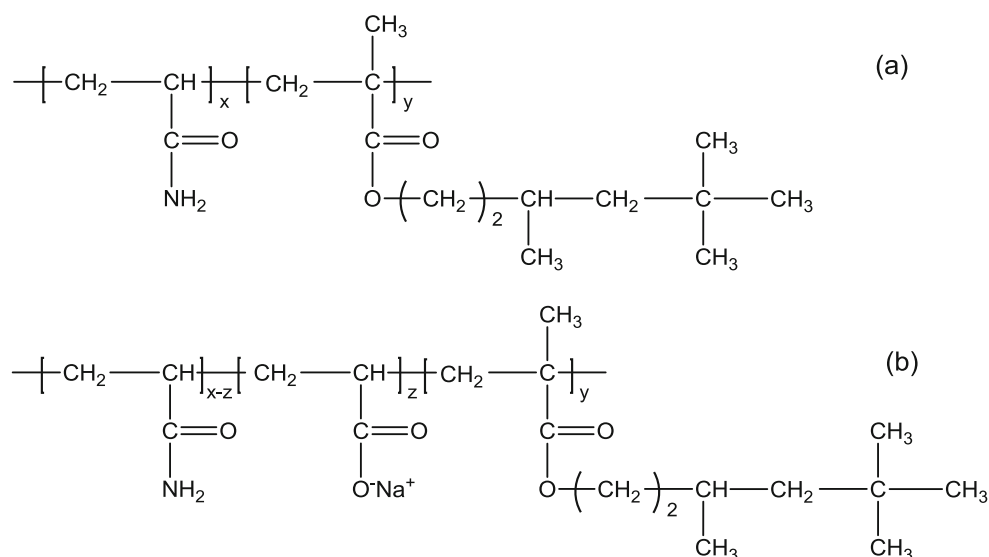
Materials

The chemical structures of polymers used in this study are shown in Fig. 1. Codes for the polymers (HAPAM and HAPAM-10N500) correspond to hydrophobically modified polyacrylamide and its partially hydrolyzed derivative, respectively. The number 10 represents the hydrolysis time in minutes, *N* is the atmosphere used during hydrolysis (*N*₂), and the number 500 is the final volume (500 mL) of the reaction mixture.

The poly(acrylamide-*co*-3,5,5-trimethylhexane methacrylate) referred to as HAPAM used in this study was kindly provided by SNF Floerger company. The molar ratio of hydrophobic groups in the HAPAM is low and fixed, in order to ensure the water solubility of polymer. In this situation, the confirmation of the molar ratio of this hydrophobic group was not possible by classical analytical techniques such as elemental analysis or NMR. Therefore, it was considered as the information of manufacturer and literature [17]. When the small amount of hydrophobic groups is not easily detectable, it is considered as the amount of hydrophobic monomer added to the reactor (0.75 mol%) [17]. All commercial grade solvents and reagents were used without additional purification.

Hydrolysis of HAPAM

HAPAM was initially dissolved in 0.1-mol/L NaCl aqueous solution, and the system was stirred at room temperature for 24 h. Polymer concentration was 2.5 times higher for HAPAM-15N100 than for HAPAM-15N500 and HAPAM-10N500, which were kept at 0.71 % (w/v) based on the molar mass of acrylamide, 0.1 mol/L, in accordance with the literature [4, 15] but with some modifications. The polymer was hydrolyzed by slow addition of NaOH aqueous solution (0.25 mol/L) into the HAPAM solution, in a reactor equipped with a magnetic stirrer, nitrogen inlet and outlet, and temperature control. The reaction mixture was prepared at different volumes (100 and 500 mL). The temperature was controlled at 40 or 50 °C for 10 or 15 min, under nitrogen atmosphere (see Table 2). Immediately after the required reaction time, NaCl (15 g for 100 mL or 25 g for 500 mL of reaction volume) was added to shield the carboxylate groups along the polymer backbone and to favor the polymer recovery from aqueous solution. Then, the reaction medium was dispersed in acetone

Fig. 1 Chemical structure of **a** HAPAM and **b** HAPAM-10N500

cooled by ice bath to precipitate the polymer, which was dried under vacuum for 24 h and then dissolved in distilled water. The conductivity of polymer solutions was measured, and the high values indicated the presence of the salt. Therefore, the polymer solutions were freeze-dried, and the white solid product obtained was washed several times with ethanol until reaching a conductivity of 20 $\mu\text{S}/\text{cm}$ in order to remove NaCl and then dried under vacuum.

NMR

The degree of hydrolysis was determined by ^{13}C nuclear magnetic resonance (^{13}C NMR) spectroscopy in D_2O . ^{13}C NMR spectra were obtained at 50 MHz in a Varian Mercury 200 MHz spectrometer. All spectra were recorded at 27 °C and incorporated 60,000 scans. Solutions were prepared by dissolving the solid polymer under magnetic stirring in D_2O , at room temperature (around 27 °C) for 24 h. Polymer concentration was 20 g/L, and relaxation time was 15 s (an accumulation time of 10 days was required to obtain better resolution for the ^{13}C spectra) [4, 7, 18].

SAXS

SAXS experiments were performed at the D11A-SAXS2 beam line of the National Synchrotron Light Laboratory (LNLS) (Campinas-SP-Brazil). A two-dimensional position sensitive detector (MarCCD) was used for the experiments, with a sample-detector distance of 1,413.9 mm and monochromatic beam wavelength of 1.488 Å. Scattering patterns were collected after an exposure time of 300 s, and scattering vector range was $0.009 < q$ (per Å) < 0.23 . The liquid samples were placed in a stainless steel sample holder closed by two mica windows, normal to the beam, and the sample cell was introduced in a chamber connected to vacuum to decrease the

parasitic scattering. A water bath was used to maintain the temperature at 25 °C. Solvent X-ray scattering was subtracted from the sample intensity, and scattering profiles were corrected for sample absorption and detector response.

SAXS measurements were performed on HAPAM and HAPAM-10N500 in the semidilute regime, using different solvents (distilled water, brine, and 0.5 mol/L NaCl). Composition of the brine was as follows: 0.02 mol/L Ca^{2+} , 0.12 mol/L Mg^{2+} , and 0.50 mol/L Na^+ . Ionic strength values for the solution used in SAXS and rheology experiments are shown in Table 1.

SLS

SLS measurements were made on a Brookhaven Instrument with an automatic goniometer table (BI-20,000) and He-Ne laser (Spectra Physics) at 632.8 nm. All measurements were conducted at room temperature (18 °C). Scattered light was measured at different angles in a range of 30° to 150°, increasing the scattering angle every 5°. The Zimm plot extrapolation procedure was applied to determine the weight average molecular weight (\overline{M}_w), radius of gyration (R_g), and second virial coefficient (A_2) of polymer samples, as per Eq. 1:

$$\frac{K_c}{R(\theta, c)} = \frac{1}{M_w} \left[1 + \frac{(R_g q)}{3} \right] + 2A_2 c \quad (1)$$

Table 1 Ionic strength of salt solutions

Salt solutions	Ionic strength
Brine	0.98
0.5 mol/L NaCl	0.50
0.5 mol/L CaCl_2	1.50

where $K=4\pi^2n^2(\text{dn/dc})^2/(N_A\lambda^4)$ is the optical contrast factor, c is the polymer concentration (mg/mL), $R(\theta, c)$ is the Rayleigh ratio, n is the refraction index of the solvent, dn/dc is the refractive index increment, N_A is the Avogadro's number, and λ is the wavelength of the laser. Moreover, q is the scattering vector expressed by $|q|=(4\pi n/\lambda_0)\sin(\theta/2)$. The refractive index increment $\text{dn/dc}=0.115$ mL/g was used for HAPAM and HAPAM-10N500 polymers, as measured by Zhu et al. [7].

For SLS measurements, the polymers (HAPAM and HAPAM-10N500) were dissolved in 1.0 mol/L NaCl and allowed to stand under magnetic stirring overnight to ensure complete dissolution. The solutions were then filtered through 0.45 μm cellulose acetate membranes (Millipore) to eliminate dust or other impurities and centrifuged at 4,000 rpm for 90 min.

Rheological measurements

Rheological measurements were carried out using a Haake RheoStress RS150 rheometer equipped with a DG41 coaxial cylinder sensor, and the temperature was maintained constant through a thermostatic bath. Rheological properties of HAPAM and HAPAM-10N500 were analyzed at different polymer concentrations, ranging from 0.5 to 5.0 g/L, in different solvents: distilled water, 0.5 mol/L NaCl, and 0.5 mol/L CaCl_2 . Solution viscosities of these polymers were measured as a function of shear rate, at a shear rate interval of 10 to 100/s and constant temperature (25 °C). The effect of temperature on the rheological behavior of polymers, at a constant shear rate (7.3/s), was studied within a range of 25 to 55 °C, at different polymer concentrations and ionic strengths.

Results and discussion

Hydrolysis of HAPAM

In the present study, HAPAM was hydrolyzed in a basic medium [19, 20] under different volumes of reaction mixture, reaction times, and temperatures. Table 2 summarizes the reaction conditions for the partially hydrolyzed polyacrylamides (HAPAM-15N100, HAPAM-15N500, and HAPAM-10N500).

The beginning of each hydrolysis reaction was qualitatively identifiable by turbidity changes (increase of turbidity) in the polymer solution under different reaction conditions. Moreover, in this case, we found that hydrolysis of a hydrophobically modified polyacrylamide solution depends critically on sodium hydroxide concentration, since it was only under alkali presence that the solution turbidity changes were observed. In the absence of the hydrolyzing agents, polyacrylamide is resistant to hydrolysis in aqueous solutions

at moderate temperatures (20 to 50 °C), but, at high temperature (for example, 93 °C), it is hydrolyzed at an appreciable rate [19, 21].

The alkaline hydrolysis acts by converting amide into carboxylate groups. Similar reaction can also happen with ester groups, converting them to carboxylate [22–25]. However, in this paper, it was considered only the hydrolysis reaction on amide groups, due to the low percentage of ester group (0.75 mol%). Another reason is the expected contribution of the long alkyl group (3,5,5-trimethylhexane) in the reduction of the methacrylate reactivity [26].

In the presence of salt, the charges of carboxylate groups are screened, diminishing the polymer solubility in water and increasing the turbidity in the polymer solution. The polymers HAPAM-15N100 and HAPAM-15N500 were obtained under reaction conditions 1 and 2, respectively, in order to determine the influence of reaction volume on hydrolysis reaction, under the nitrogen atmosphere, when the volume of the reaction mixture was altered from 100 mL (HAPAM-15N100) to 500 mL (HAPAM-15N500). In other words, the polymer concentration was decreased at constant NaOH concentration, resulting in a degree of hydrolysis of 49 %. This value can be attributed to an increase in the $[\text{NaOH}]/[\text{polymer}]$ ratio [19]. In order to obtain a polymer with a lower degree of hydrolysis than that achieved for HAPAM-15N500, a third hydrolysis reaction was carried out under condition 3, resulting in HAPAM-10N500 with a 45 % degree of hydrolysis. The degree of hydrolysis for HAPAM-15N500 and HAPAM-10N500 is close, this suggests that the changes of reaction time and temperature are still small to significantly affect the degree of hydrolysis (DH), maintaining NaOH concentration and polymer concentration constants of third reaction compared to second reaction. In summary, the HAPAM and HAPAM-10N500 samples were chosen to the study of physicochemical properties in solution, in order to evaluate whether the associative polymer containing low content of hydrophobic alkyl chain with high degree of hydrolysis continues to show improved rheological properties and better stability with respect to salts.

^{13}C NMR

Figures 2 and 3 depict the ^{13}C NMR spectra of HAPAM and HAPAM-10N500, respectively. Figure 2 shows peaks at 180, 41, and 36 ppm, corresponding to carbonyl groups (c), methine carbon (b), and methylene carbon (a) of the acrylamide unit, respectively [4]. Carbonyl groups of the hydrophobic unit could not be identified due to the low hydrophobic content of HAPAM [7].

The ^{13}C NMR spectrum of HAPAM-10N500 confirms the hydrolysis reaction (Fig. 3). This is due to the presence of an additional peak at 182–184 ppm resulting from carbonyl

Table 2 Reaction conditions used to obtain partially hydrolyzed hydrophobically modified polyacrylamides at various degrees of hydrolysis (DH)

Polymer	Condition	Atmosphere	T (min)	T (°C)	V (mL)	DH (%)
HAPAM-15N100	1	Nitrogen	15	50	100	12
HAPAM-15N500	2	Nitrogen	15	50	500	49
HAPAM-10N500	3	Nitrogen	10	40	500	45

DH is determined by ^{13}C NMR

groups in the acrylate units, which were absent in the polymer precursor (HAPAM) [27].

According to previous studies [7, 28], ^{13}C NMR spectroscopy is the preferred method to accurately determine the DH of partially hydrolyzed hydrophobically modified polyacrylamide. DH of HAPAM-10N500 was determined using Eq. 2, where A_{COO^-} and A_{CONH_2} are the integrated peak areas at 182–184 and 179–181 ppm corresponding to the carbonyl carbons of acrylate and acrylamide units, respectively [4, 29]. The result of the DH for the HAPAM-10N500 is listed in Table 2.

$$\text{DH (\%)} = 100 \left[\frac{A_{\text{COO}^-}}{A_{\text{CONH}_2} + A_{\text{COO}^-}} \right] \quad (2)$$

SAXS

SAXS measurements were performed to evaluate the polyelectrolyte character of HAPAM-10N500 and to provide useful information on the chain conformation in the semidilute regime. The presence of charges along the hydrophobically modified hydrolyzed polyacrylamide (HAPAM-10N500)

chains significantly modifies their properties with respect to the neutral polymer (HAPAM). In the absence of salt, all aqueous HAPAM-10N500 solutions from 5.0 to 20.0 g/L showed scattering peaks in the q -SAXS range. This behavior is illustrated in Fig. 4, where $I(q)$ is plotted as a function of q for HAPAM-10N500.

In the semidilute regime, the peak observed for polyelectrolyte solution salt-free in SAXS experiments may be explained using the isotropic model by de Gennes et al. [30, 31]. In this model, the polymer chain is formed by a succession of “electrostatic blobs (ξ_e)” each of size ξ_e . For a spatial scale (r) less than ξ_e ($r < \xi_e$), inside the blobs, the thermal energy dominates over electrostatic interaction and the chain conformation is a self-avoiding walk in a good solvent [32]. Otherwise, for r larger than ξ_e ($r > \xi_e$), the electrostatic interaction dominates thermal energy; therefore, the chains of electrostatic blobs are locally stiff (a directed random walk) [33]. The electrostatic repulsion between carboxylate units on HAPAM-10N500 structures the solution such that the distance to the nearest chain is close to the correlation length (ξ). Therefore, the local structure of the HAPAM-10N500 solutions is the reason to appearance of a peak in their scattering

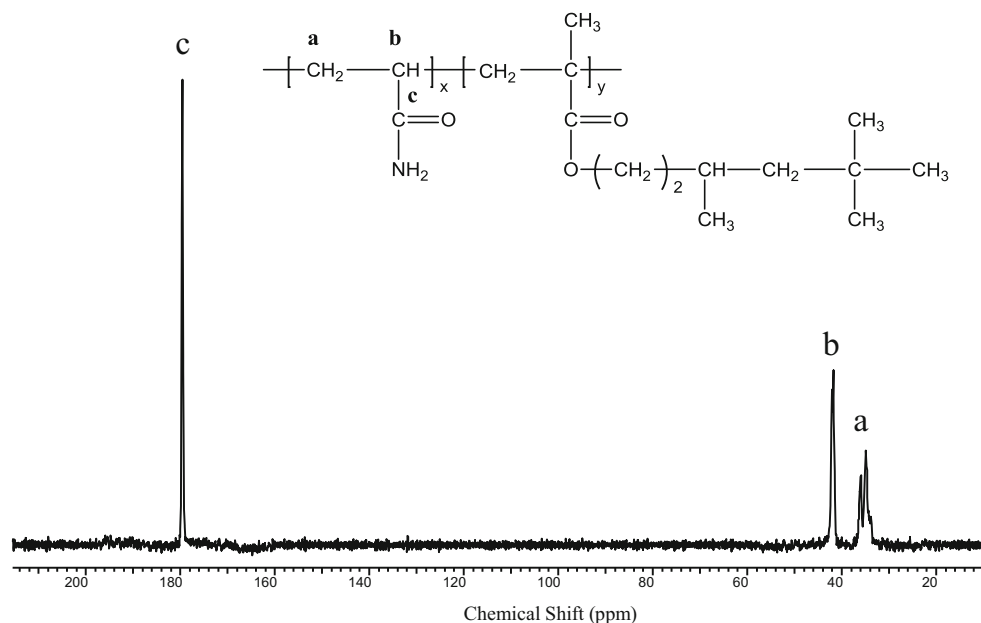
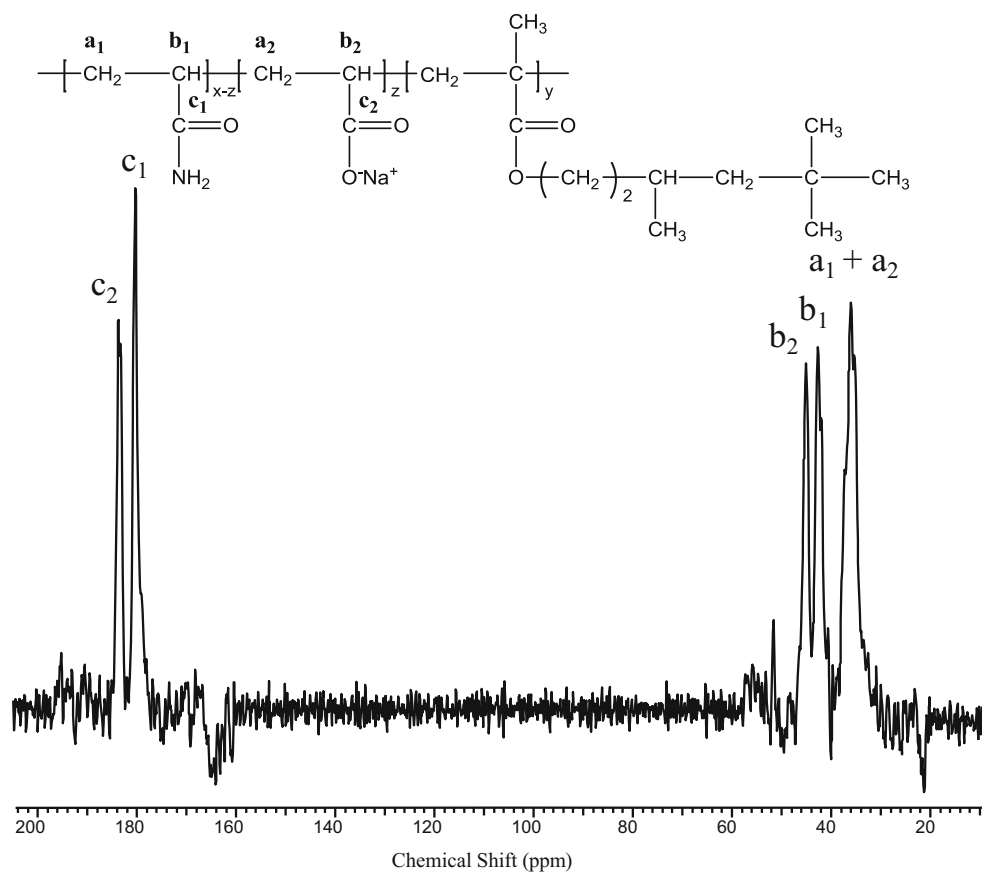
Fig. 2 ^{13}C NMR characterization of HAPAM

Fig. 3 ^{13}C NMR characterization of HAPAM-10N500



function. These SAXS results highlight the polyelectrolyte character of this hydrophobically modified polyacrylamide with high degree of hydrolysis.

As can be seen from Fig. 4, the peak position depends on polyelectrolyte concentration. The wave vector position at maximum scattering intensity, q_{\max} , shifts toward higher

scattering vector values with the increase in the polymer concentration. This profile in SAXS suggests that correlation length decreases with the rise in polyelectrolyte concentration, according to Bragg's law ($\xi = 2\pi/q_{\max}$).

Figure 5 illustrates the behavior of the HAPAM at different polymer concentrations.

Fig. 4 Plot of the scattered intensity $I(q)$ as a function of the scattering vector q for HAPAM-10N500 in aqueous solution with different polymer concentrations at 25 °C

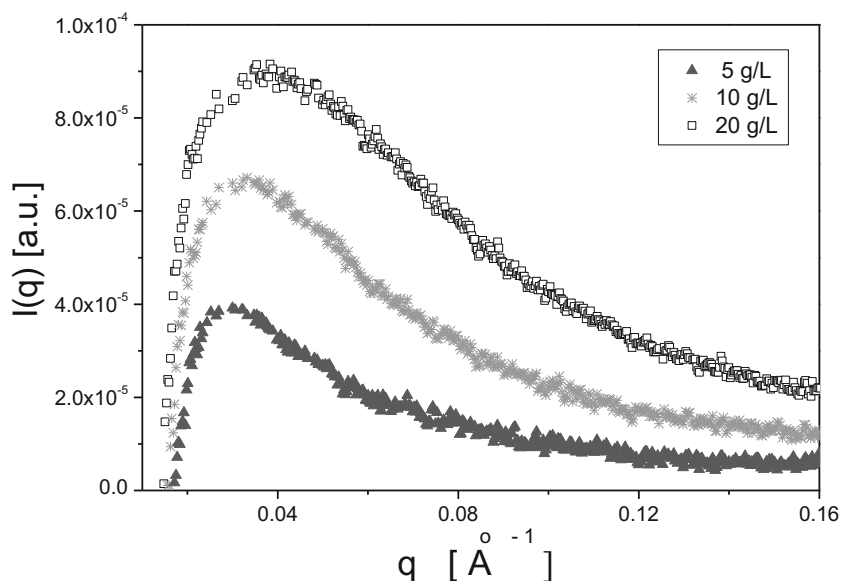
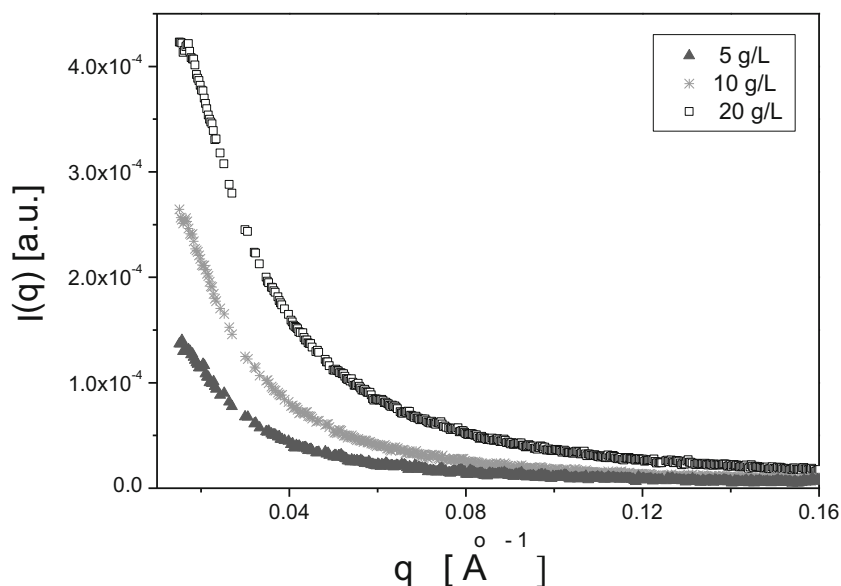


Fig. 5 Plot of the scattered intensity $I(q)$ as a function of the scattering vector q for HAPAM in aqueous solution with different polymer concentrations at 25 °C



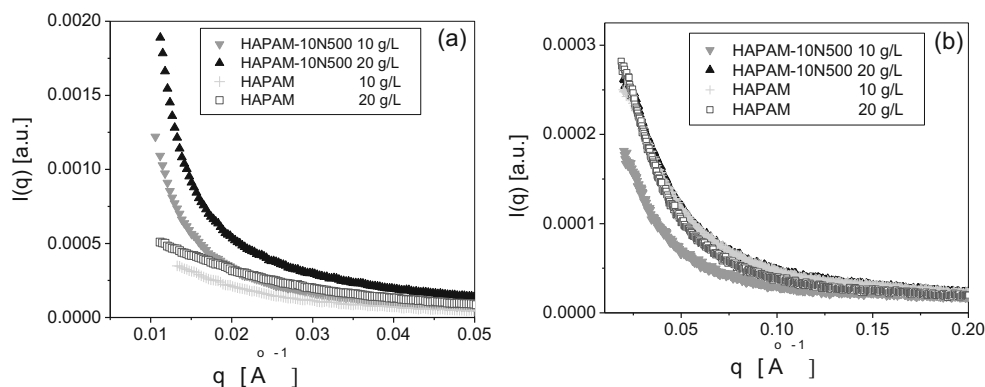
As expected, for all polymer concentrations studied and the q -SAXS range investigated, no scattering peak was observed because HAPAM is a neutral polymer (zero hydrolysis degree). $I(q)$ decreased with the increase in q value, typical behavior of an uncharged polymer. These results clearly demonstrated that HAPAM chains exhibit a coil conformation, while HAPAM-10 N500 shows an extended conformation.

Figure 6a, b show the effect of brine and 0.5 mol/L NaCl, respectively, in the SAXS profile for HAPAM and HAPAM-10N500.

For both solvents, brine and 0.5 mol/L NaCl, the polyelectrolyte peak disappears for all polymer concentrations investigated. At ionic strengths studied, the profile of $I(q)$ versus q for HAPAM-10N500 is similar to that of HAPAM. This is because the addition of electrolytes such as NaCl or CaCl_2 to a polyelectrolyte screens out intermolecular electrostatic interactions, due to the decrease in the electrostatic potential and electrical double-layer compression. Therefore, the local structure is replaced by a disordered coil-like chain, behaving like a neutral polymer.

As can be seen from Fig. 6a, HAPAM-10N500 shows higher $I(q)$ at small q values than HAPAM in brine, indicating a synergistic effect due to the effects of charges and association of hydrophobic groups. HAPAM-10N500 contains 45 % of carboxylic groups (COO^-) and a relatively small content of hydrophobic groups (3,5,5-trimethylhexane methacrylate) along the polymer chain. Thus, the formation of aggregates in brine may be favored as a result of the following two effects: (i) divalent cations such as Ca^{2+} and Mg^{2+} that can promote bridging between COO^- of different polymer chains and (ii) interactions between hydrophobic blocks that would be facilitated by reduction of the negative charges on the polymer chain due to the addition of salt. Moreover, $I(q)$ values for HAPAM-10N500 and HAPAM in brine were greater than in 0.5 mol/L NaCl (see Fig. 6b). Brine displays greater ionic strength than the 0.5 mol/L NaCl solution, producing a bridging between carboxylate groups and more hydrophobic interactions. It is well known that these interactions depend only on ionic strength, regardless of the nature of the ionic species [10, 34]. Consequently, in brine, the

Fig. 6 Plot of the scattered intensity $I(q)$ as a function of the scattering vector q for HAPAM-10N500 and HAPAM in solution aqueous with different polymer concentrations in **a** brine and **b** 0.5 mol/L NaCl ($T=25$ °C)



aggregates display higher hydrodynamic volume than in NaCl solution, leading to greater X-ray scattered intensity [35–37].

Furthermore, $I(q)$ values of HAPAM for different polymer concentrations in 0.5 mol/L NaCl are similar. This behavior can be attributed to two factors: (i) few hydrophobic groups and (ii) low ionic strength of the medium.

SLS

SLS measurements provide information about molecular properties of the polymers in solution [10]. SLS results were obtained in 1.0 mol/L NaCl as a solvent for HAPAM and HAPAM-10N500 in the dilute regime that is below overlap concentration (c^*). The Zimm plot method was used to determine weight average \overline{M}_w , A_2 , and R_g . The Zimm plots of HAPAM and HAPAM-10N500 are shown as supplementary materials. The results are listed in Table 3.

\overline{M}_w for HAPAM and HAPAM-10N500 were very close, indicating that degradation did not occur during hydrolysis in the absence of oxygen and temperature studied. This corroborates with data reported by Muller et al., which showed that molecular weight degradation is strongly dependent on the presence of both oxygen and residual impurities and/or elevated temperature [38].

Quality of the solvent could be estimated from the value of the A_2 [39, 40]. According to results shown in Table 3, HAPAM and HAPAM-10 N500 exhibit positive values for A_2 , indicating that 1.0 mol/L NaCl is a good solvent, but this solvent is more appropriate to HAPAM-10N500. This is likely due to the good polymer-solvent interactions caused by the introduction of carboxyl groups on the polymer backbone [41]. In addition, a slight decrease in the A_2 value of HAPAM in 1.0 mol/L NaCl aqueous solution compared with that of HAPAM-10 N500 demonstrates that the HAPAM is not well solvated by the NaCl aqueous solution. This result can be attributed to the more significant hydrogen bonds from the amide functional groups and possible interactions between hydrophobic groups on polymer chains due to the reduction of the solvent quality. Chen and Ayres reported the dynamic light scattering (DLS) characterization of a poly(*N*-alkyl urea peptoid-*g*-poly(styrene-*b*-acrylic acid) in 1.0 mol/L NaCl solution at pH 8 in order to evaluate the salt effect on micelles size. The results indicated the presence of particles with an average diameter of 479 nm, suggesting that the micelles were formed by aggregating several polymer chains in solution

instead of individual polymer chain, suggesting that the self-assembly is driven through hydrogen bonding interactions from the urea functional groups [42]. The R_g for HAPAM-10N500 was greater than that of HAPAM indicating again that 1.0 mol/L NaCl is a better solvent to the former.

Based on SLS data, we determined the overlap concentration (c^*) for HAPAM-10N500 and HAPAM, using Eqs. 3 and 4. The $c_{R_g}^*$ and $c_{A_2}^*$ provide a good thermodynamic definition of polymer overlap concentrations [43, 44]. HAPAM-10N500 has a lower $c_{R_g}^*$ and $c_{A_2}^*$ when compared to HAPAM (see Table 3), possibly because chain dimensions for HAPAM-10N500 are greater than those of HAPAM, meaning that concentrations at which polymer chains begin to touch each other are lower.

$$c_{R_g}^* = \frac{3\overline{M}_w}{4\pi N_A R_g^3} \quad (3)$$

$$c_{A_2}^* = \frac{1}{A_2 \overline{M}_w} \quad (4)$$

where N_A is the Avogadro's number.

Rheological behavior

Effects of polymer concentration and shear rate

Rheological behavior of aqueous HAPAM and HAPAM-10N500 solutions, at different polymer concentrations, in distilled water at 25 °C are shown in Fig. 7a, b, respectively. Rheological properties of polymer solutions were measured in order to gain insight into the structure and conformation of polymers.

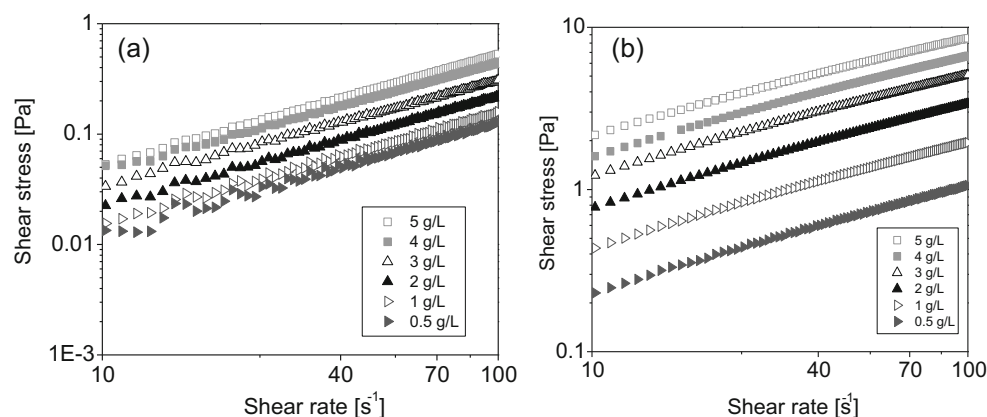
It is possible to observe that the shear stress increased with both shear rate and polymer concentration in the medium. This effect was more significant for the hydrolyzed derivative because of the electrostatic repulsion between carboxylate groups in aqueous medium.

The polymer solutions exhibit a relationship between shear stress and shear rate that follows a power law ($\tau = K\dot{\gamma}^n$), where n (flow behavior index) indicates the deviation of fluid from the Newtonian model. For pseudoplastic fluids, n must have values between 0 and 1, and for Newtonian fluids, n is equal to 1. Table 4 shows the R^2 (linear correlation coefficient) and n

Table 3 Physicochemical properties of the polymers HAPAM and HAPAM-10N500

Polymer	\overline{M}_w (g/mol)	A_2 (cm ³ mol/g ²)	R_g (nm)	$c_{R_g}^*$ (g/L)	$c_{A_2}^*$ (g/L)
HAPAM	2.63×10^6	2.3×10^{-5}	80.6	2.0	16.5
HAPAM-10N500	1.79×10^6	2.4×10^{-4}	109.6	0.5	2.3

Fig. 7 Shear stress versus shear rate for **a** HAPAM and **b** HAPAM-10N500 at different polymer concentration, in distilled water, at 25 °C



values obtained from the flow curve for HAPAM and HAPAM-10N500 in a shear rate range of 10 to 100/s.

The R^2 values for HAPAM and HAPAM-10N500 were very close to 1, indicating a good fit of the mathematical equation curve defined by the power law to experimental data. The n values for HAPAM and HAPAM-10N500 solutions demonstrated that, in the shear range evaluated, the fluids exhibit Newtonian behavior (n very close to 1) and shear thinning ($0 < n < 1$), respectively.

Figure 8a, b shows apparent viscosity as a function of shear rate for aqueous HAPAM and HAPAM-10N500 solutions, respectively, at different polymer concentrations in distilled water at 25 °C.

As can be seen, the apparent viscosity increases markedly with polymer concentration for HAPAM-10N500. Otherwise, viscosity of HAPAM solutions increased slightly with polymer concentration. Furthermore, for the same polymer concentration, the HAPAM-10N500 sample shows high viscosity when compared to HAPAM. Viscosity gain recorded

for the HAPAM-10N500 solution may be primarily a result of electrostatic repulsion among carboxylate groups (COO^-), causing an increase in hydrodynamic volume. This rheological behavior is perfectly in line with SAXS results, which showed that HAPAM-10N500 displays an extended conformation and HAPAM, a coil conformation in a semidilute regime. These figures also confirm Newtonian and pseudoplastic behavior for HAPAM and HAPAM-10N500 solutions, respectively, in a shear rate range of 10 to 100/s, as indicated by the power law.

Rheological properties of the polymers studied here depend on degree of hydrolysis and intermolecular and intramolecular association-dissociation under shear rate. At rest and at low shear rate, the polyelectrolyte HAPAM-10N500 shows a local structure due to electrostatic repulsion among carboxylate groups. However, with increasing shear rates, the extended polymer chains align lengthwise in the direction of shear. This leads to reduced internal resistance against flow and, consequently, lower viscosity (pseudoplastic behavior). It is important to note that ionic polymers display preferential alignment in the direction of flow under shear. Villetti et al. [45] used SAXS coupled to shearing device to show that Na-hyaluronate (Na-Hy), a polyelectrolyte with low charge density and small intrinsic persistence length, exhibits no scattering peak in the q -SAXS range when at rest. However, as the shear rate increases to a maximum, the scattering peak is magnified and clearly reveals the expected polyelectrolyte nature of Na-Hy. At high shear, the chains adopt preferential alignment in the direction of shear.

Effect of ionic strength

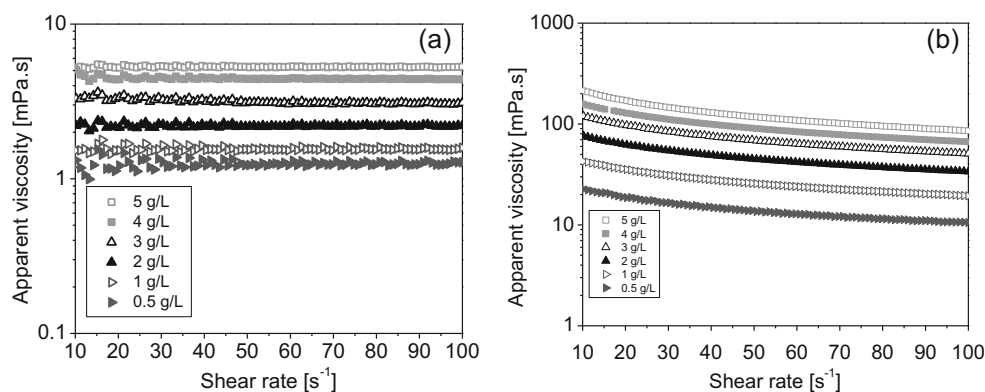
The effect of ionic strength on rheological behavior of the HAPAM and HAPAM-10N500 solutions at 5 g/L and 25 °C can be seen in Fig. 9a, b, respectively.

In the shear rate range of 10 to 100/s, the viscosities of HAPAM solutions tend to rise slightly with the increased ionic strength of the medium. The highest viscosity occurred for an

Table 4 The R^2 and n values obtained from the power law applied to the flow curve for aqueous HAPAM and HAPAM-10N500 solutions at 25 °C

Polymer	c [g/L]	R^2 values	n values
HAPAM	5	0.998	0.99
	4	0.980	0.98
	3	0.998	0.95
	2	0.998	0.99
	1	0.997	0.99
	0.5	0.990	1.01
HAPAM-10N500	5	0.998	0.59
	4	0.997	0.61
	3	0.998	0.61
	2	0.998	0.63
	1	0.988	0.64
	0.5	0.998	0.65

Fig. 8 Apparent viscosity plotted as a function of shear rate for **a** HAPAM and **b** HAPAM-10N500 at different polymer concentrations, in distilled water, at 25 °C



ionic strength value equals to 1.5, indicating that intermolecular interactions among hydrophobic groups are more favored in a solution with greater ionic strength. Similar results were found by Feng et al.. They reported the effects of NaCl and CaCl₂ on viscosity of associative polyacrylamide containing 1.0 mol% of octyl alkyl group. Viscosity was higher with addition of CaCl₂ than that of NaCl for the same molar concentration, indicating that the effect of salts on the hydrophobic interactions depends only on the ionic strength [10].

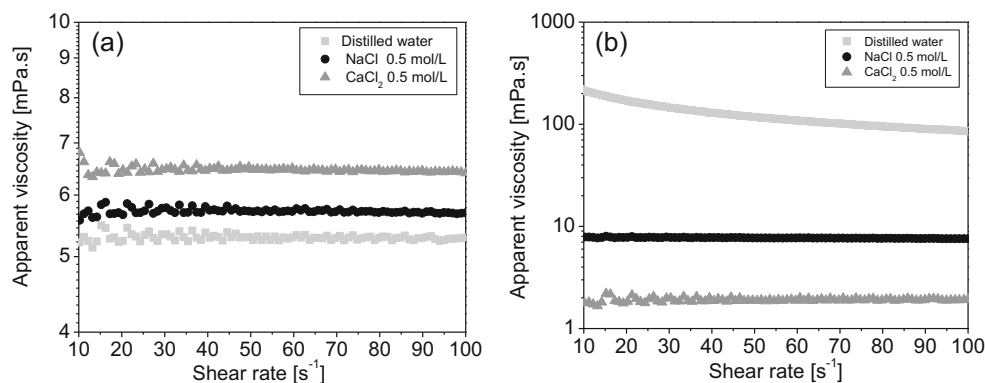
For the HAPAM-10N500 polyelectrolyte, in distilled water at 10/s, a viscosity around 200 mPa s and pseudoplastic behavior with the increase of shear rate was obtained (Fig. 9b). This result suggests that electrostatic repulsions were more significant than interactions among hydrophobic groups, likely due to the high degree of hydrolysis. Apparent viscosity for HAPAM-10N500 solutions demonstrated more significant change in the presence of salt. Viscosity declined dramatically with increasing ionic strength of the medium owing to partial screening out of the charges of carboxylate groups and low hydrophobic content on the polymer chain. The solutions showed Newtonian behavior in the shear rate range studied. The observed results are in agreement with those reported by Biggs, Selb, and Candau [15]. They showed that the high incorporation of ionic groups (such as carboxylate groups) may lead to absence of any hydrophobic associative behavior

due to the increased overall hydrophilic character of the polymer.

The properties of HAPAM-10N500 in aqueous solution studied here were compared to those of partially hydrolyzed polyacrylamide (HPAM) reported in the literature [16, 27, 46, 47]. In our experimental conditions, it was observed that viscosity values of HAPAM-10N500 with high degree of hydrolysis significantly decreased with increasing ionic strength of the medium. The favoring of the hydrophobic interactions in partially hydrolyzed hydrophobically modified polyacrylamides depends on the macromolecular architecture, degree of hydrolysis, polymer concentration, and ionic strength as reported by Feng Y, Noda T, and Biggs S [10, 15, 48, 49]. In our case, HAPAM-10N500 exhibited similar rheological behavior to HPAM. However, a significant disadvantage of HPAM is its higher sensitivity to salts when compared to partially hydrolyzed hydrophobically modified polyacrylamide, especially at higher hydrophobic group contents [2]. Moreover, insolubility problems of HPAM can arise when its degree of hydrolysis is very high.

McCormick, Middleton, and Cummins reported that the NaAMB-25 terpolymer containing acrylamide (94.5 mol%), *n*-decylacrylamide (0.5 mol%), and sodium 3-acrylamido-3-methylbutanoate (25 mol%), with high degree of hydrolysis and above polymer concentration of 1.5 g/L, initially, results

Fig. 9 Apparent viscosity as a function of shear rate for **a** HAPAM and **b** HAPAM-10N500 at 5 g/L in different solvents at 25 °C



in a more expanded chain with high apparent viscosity at low solution ionic strength. In this system, apparently, the high degree of hydrolysis effectively prevents hydrophobic aggregation in a medium with NaCl concentration lower than 0.17 mol/L, suggesting insufficient salt amount to effectively reduce electrostatic repulsions. On the other hand, coil collapses with increasing ionic strength of the medium up to 0.17 mol/L NaCl, decreasing its apparent viscosity. However, an increase in viscosity was observed above 0.17 mol/L NaCl [14].

Viscosity for HAPAM-10N500 with high degree of hydrolysis was higher than that recorded for the HAPAM solution in the presence of 0.5 mol/L NaCl. However, an opposite behavior was observed for these polymers in 0.5 mol/L CaCl_2 . These results suggest that the charges on polyelectrolyte may not have been fully screened by monovalent cations of NaCl. On the other hand, HAPAM-10N500 chain is further collapsed in solution with higher ionic strength ($\mu=1.5$, corresponding to 0.5 mol/L CaCl_2). This study showed the importance of the presence of charges to obtain thickening property in a given polymer concentration and ionic strength [15, 50, 51].

Effect of temperature

The effect of temperature on the viscosity of HAPAM and HAPAM-10N500 solutions is shown in Fig. 10a, b, respectively.

For both polymers, there is a linear relation between $\ln \eta$ and $1/T$, in accordance with the Arrhenius equation, for all polymer concentrations and solvents studied. The decline in viscosity with increasing temperature is a result of greater mobility of polymer chains, leading to reduced intermolecular interactions.

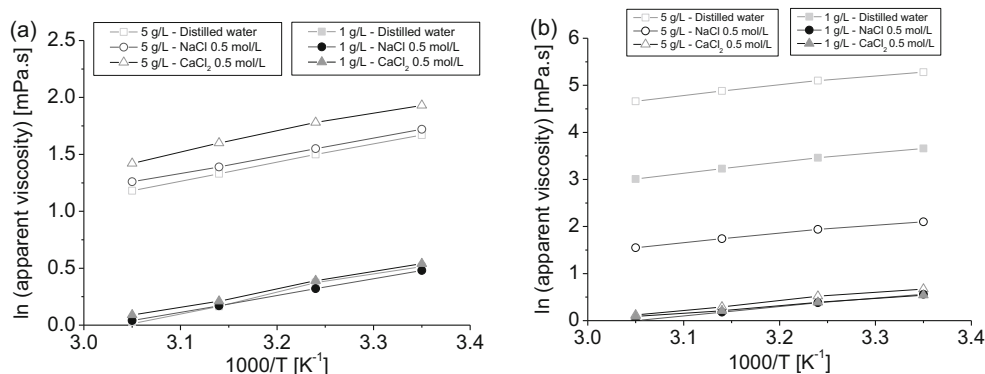
Moreover, a slightly different behavior was observed for HAPAM-10N500 solutions compared to HAPAM solutions owing to the high degree of hydrolysis, as per Fig. 10b. These results are in agreement with the observed values for the activation energy (curves not shown here) of these polymers in the systems evaluated. In the semidilute regime, the values of activation energy (E_a) for HAPAM-10N500 in distilled water,

0.5 mol/L NaCl, and 0.5 mol/L CaCl_2 were, respectively, 16.7, 14.8, and 15.1 kJ/mol, indicating reduction of electrostatic repulsions in the presence of salt. For solutions of HAPAM, the values of E_a in distilled water, 0.5 mol/L NaCl, and 0.5 mol/L CaCl_2 were, respectively, 13.8, 12.3, and 13.7 kJ/mol. Therefore, the difference between the values of activation energy for HAPAM-10N500 and HAPAM is due to the presence of carboxylate groups, which are absent in HAPAM. In general, the values of E_a for HAPAM were relatively low and close to each other, indicating that the physical interactions (hydrophobic aggregates) involved are very weak interactions and can be easily undone. The values of E_a for HAPAM and HAPAM-10N500 polymers in semidilute regime were near those found in the literature related to comparison between natural and synthetic polymers unmodified and hydrophobically modified derivatives [52, 53].

Conclusions

The present study investigated the physicochemical properties of a HAPAM (poly(acrylamide-co-3,5,5-trimethylhexane methacrylate)) and its partially hydrolyzed derivative with high degree of hydrolysis in different ionic strengths of the medium. ^{13}C NMR confirmed the hydrolysis of the hydrophobically modified polyacrylamide. SAXS measurements highlighted the polyelectrolyte character of the HAPAM-10N500. SAXS results demonstrated that HAPAM chain exhibits a coil conformation, while HAPAM-10N500 shows an extended conformation with a local order. $I(q)$ values for HAPAM and HAPAM-10N500 solutions depended on polymer concentration and ionic strength of the medium. SLS results showed that HAPAM-10N500 has a lower overlap concentration when compared to HAPAM. The elevated degree of hydrolysis of HAPAM-10N500 significantly modifies its properties in relation to the neutral polymer. HAPAM containing low content of hydrophobic alkyl chain (C9) showed poor viscosity contribution in water and a slight increase in viscosity in presence of salt, which would be expected due to hydrophobic associations. On the other hand,

Fig. 10 $\ln \eta$ versus $1/T$ for **a** HAPAM and **b** HAPAM-10N500 solutions, at 1 and 5 g/L polymer concentration in different solvents at shear rate of 7.3/s



the HAPAM-10N500 showed a high viscosity in water due to high degree of hydrolysis. Moreover, in the presence of salt (0.5 mol/L NaCl), the viscosity of HAPAM-10N500 was higher when compared to HAPAM. This behavior can be attributed to the synergistic combination of two factors: (i) the presence of charges that were not completely screened along the backbone and (ii) favoring of hydrophobic interactions. These rheological results demonstrated that the solution viscosity of the polymers studied depends on several factors, including electrostatic persistence length of the polymer, polymer concentration, ionic strength, and temperature.

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