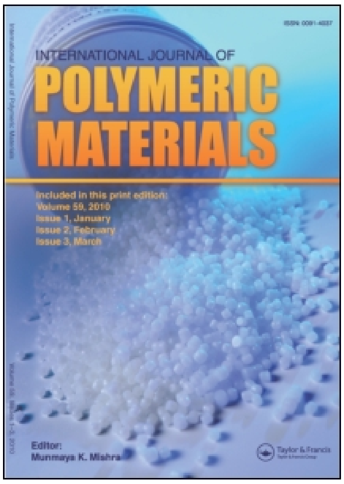

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Rheological Behaviour of Poly (Acrylamide-G-Propylene Oxide) Solutions: Effect of Hydrophobic Content, Temperature and Salt Addition

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The viscosity of hydrophobically modified polyacrylamide was investigated as a function of polymer concentration in aqueous and in salt solutions, and also as a function of temperature. The graft copolymers were constituted of polyacrylamide backbone and different amount of hydrophobic poly(propylene oxide) graft chains. Measurements of intrinsic viscosities have been performed by using a Contraves low-shear LS-40 rheometer. From these results, a dependence of the intrinsic viscosity of the polymer solution with the molecular weight was observed, where an increase of the latter resulted in higher intrinsic viscosity. In this case, the effect of the molecular weight was more emphasized than the effect caused by the slightly different degrees of hydrophobic incorporation. When enhancing the temperature, it was not verified a significant change on the reduced viscosities of the copolymer solutions and the graft chain length was also observed.

Keywords: Acrylamide; propylene oxide; hydrophobic interactions; rheology

INTRODUCTION

Recently, the control of aqueous viscosity with polymeric molecules has become an area of great industrial importance [1]. Copolymers

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exhibiting associative thickening behavior in aqueous media have become increasingly important in the formulation pharmaceuticals, cosmetics, agricultural chemicals, and coatings [2]. One example of these materials is the hydrophobically modified water-soluble polymers, which are used in many oilfield applications, such as several enhanced oil recovery (EOR) processes [1, 3–6], since those polymers are able to reduced the mobility of the injected fluid by increasing the viscosity of the aqueous phase [7–10].

The water-soluble hydrophobically associating polymers are very similar to conventional water-soluble polymers, except that they have a small number of hydrophobic groups incorporated into the polymer backbone [8,11]. In such copolymers the presence of only small quantities of the hydrophobic comonomer (< 1 mol%) is sufficient to alter the solution rheological properties [1], turning their rheological properties markedly different from those of the unmodified parent polymers [12].

In the presence of water, intra or intermolecular associations occur to minimize the water-hydrophobe contact [5]. In aqueous solutions, above a critical overlap concentration c^*, the hydrophobic groups of these polymers can self-associate [13, 14] to minimize their exposure to the solvent, and these intermolecular associations cause the formation of physical linkages between the copolymer chain [1] and result in an increase in hydrodynamic volume causing an increased solution viscosity [8, 15]. At very low concentrations, considered as an infinite dilution, the hydrophobic interaction is expected to be only intrachain [14] and consequently, the intrinsic viscosity $[\eta]$ of a hydrophobically modified polymer would be lower than that of the unmodified one [12]. Hence, the critical overlap concentration c^* often appears well below the critical entanglement concentration of the unmodified or parent polymer of equivalent molecular weight [3].

The rheological properties of polymer solutions play an important role in determining their effectiveness. These properties depend on the solubility characteristics of the polymers and may be affected by the presence of chemical substances, for example, salts [10], once they can lead to changes in the chemical and physical nature of the polymer molecule.

The purpose of this work is to investigate the viscosity of hydrophobically modified polyacrylamide as a function of polymer concentration in aqueous and salt solutions, at different temperatures. The graft copolymers are constituted of different hydrophobe chains contents, where the hydrophobe group is represented by chains of poly(propylene oxide)(PPO).

EXPERIMENTAL

Materials

Polyacrylamide and graft copolymers were prepared previously, as well as the characterization of the graft chain contents by ^{13}C NMR [16].

Molecular Weight Characterization

Molecular weights were obtained from size exclusion chromatography (SEC) of polymer azide aqueous solutions with 0,1M $NaNO_3$ using a Waters GPC with refractive index detector.

Rheological Measurements

Polymer solutions for rheological measurements were made by successive dilutions of polyacrylamide and poly(acrylamide-g-propylene oxide) in aqueous (deionized H_2O) and in salt (0,1 M NaCl) solutions, in order to study the influence of adding an ionic substance (NaCl).

The apparent viscosities of the polymer solutions as a function of the shear rate were measured using a Contraves low-shear LS-40 rheometer, at various concentrations of polymer and over a temperature range of 10–50°C. The intrinsic viscosities of the polymers were determined using standard techniques [17].

RESULTS AND DISCUSSION

Table I shows the composition and the molecular weights of the polymers studied, as well as the results of intrinsic viscosity $[\eta]$ in

TABLE I Compositional data and results of intrinsic viscosity for the polymers studied

Polymer	*Molecular weight of the graft chain (PPO)*	*Graft chain content*[14] *(mass%)*(a)	*Number average molecular weight (Mn)*(b)	*Intrinsic viscosity [η] (dL/g) (aqueous solution)*	*Intrinsic viscosity [η] (dL/g) (salt solution, 0,1 M NaCl)*
PAAm	–	–	9,450	0.52	0.49
COP 4	400	4.7	10,700	0.64	0.51
COP 5	1000	5.7	22,900	0.79	0.74
COP 6	1000	6.1	37,500	0.88	0.59

(a) Determined from ^{13}C – NMR[16].
(b) Determined from SEC[16].

TABLE II Intrinsic viscosities and critical concentrations of the polymer solutions

Polymer	*Intrinsic viscosity [η] (dL/g) (aqueous solution)*	*Instrinsic viscosity [η] (dL/g) (salt solution, 0,1 M NaCl)*	*Critical concentration, c^* (g/dL) (aqueous solution)*	*Critical concentration, c^* (g/dL) (salt solution, 0,1 M NaCl)*
PAAm	0,52	0,49	1,33	1,02
COP 4	0,64	0,51	1,45	–
COP 5	0,79	0,74	1,11	0,61
COP 6	0,88	0,59	0,65	0,41

aqueous and in salt solutions. The copolymers were synthesized *via* solution polymerization and therefore, the molecular weight obtained were relatively low and a control of the degree of incorporation of hydrophobe was hindered [16].

In order to determine whether the viscometric study was on a dilute or semi-dilute regime of concentration, it was investigated experimentally the critical overlap concentration (c^*) of each polymer solution, both in aqueous and in salt solutions. The values obtained are shown on Table II. It can be infered that in aqueous solutions, the higher the intrinsic viscosity of the copolymer, the higher the hydrodynamic volume and consequently, the lowest the critical overlap concentration.

Effect of Hydrophobe Content *Versus* Molecular Weight

It is well known that the solubility of water-soluble associating polymers decreases as the hydrophobe content increases [18].

Nevertheless, below a critical concentration c^* (the overlap concentration), the introduction of hydrophobic groups results in a slight decrease in the reduced viscosity, due to intramolecular association, which also reduces intrinsic viscosity and leads to the contraction of the polymer chain [8, 12]. Although the increased number of hydrophobic groups on the polymer backbone can lead to intramolecular interactions, no remarkable decrease in intrinsic viscosities of the aqueous solutions were evident on Table I. The results indicate that, in this case, the influence of the molecular weight is more significant than that of the slight differences of the hydrophobe content. Therefore, the higher the molecular weight, the larger will be the hydrodynamic volume and consequently, higher intrinsic viscosity.

Effect of Salt Addition

The addition of NaCl to the copolymer solutions, on the other hand, decreases the intrinsic viscosity (Tab. I), since the water-structuring effect of NaCl allows hydrophobic association and this association occurs in order to minimize their exposure to the solvent. Brady and co-workers [8] found that for solutions of polymers which contain an appreciable amount of hydrophobic monomer, the addition of salt would increase the aggregation of hydrophobes. As a consequence, if the hydrophobic associations arise essentially from intrachain nature, the copolymer coil dimensions would be expected to diminish after any increase in the number of interactions. This agree with the results showed on Table I. It also has to be noted that the salt solution of COP 6, which has the greatest hydrophobe content, presented a drastic drop of the intrinsic viscosity, likely due to intrachain association.

Effect of Temperature

Temperature effects on the rheology of the copolymers solutions (3.8 g/dL) were investigated, in a semi-dilute regime, considering their reduced viscosities, η_{red}, as a function of temperature over a range of 10–50°C. In Figures 1 and 2, the reduced viscosities as a function of temperature are shown for the aqueous and the salt solutions, respectively.

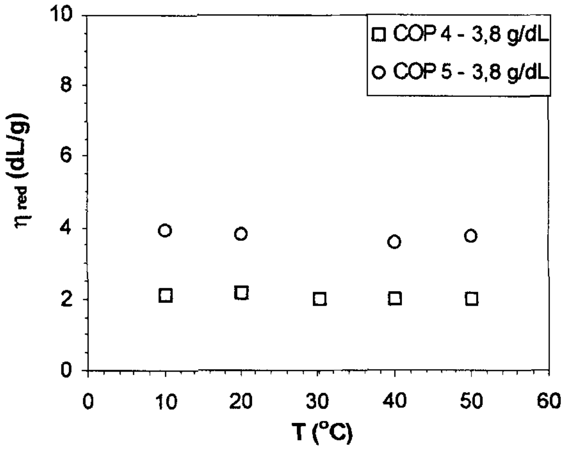

FIGURE 1 Reduced viscosity as a function of temperature for polymer aqueous solutions.

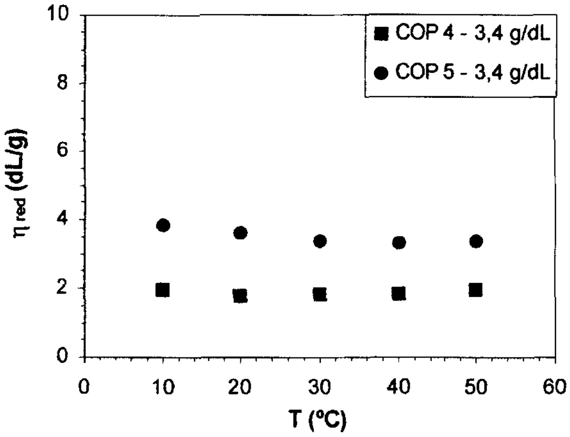

FIGURE 2 Reduced viscosity as a function of temperature for polymer salt solutions (0,1 M NaCl).

When studying the solution behaviour of polyacrylamide grafted with poly(ethylene oxide-co-propylene oxide), Sicco de Vos and coworkers [19] noticed that these water-soluble polymers are expected to associate at elevated temperatures, owing to the decreasing solvation of the polyether grafts. Hence, considering that the temperature enhancement causes a PPO solubility decrease, in a semi-dilute region, we expect to observe an increase on the reduced viscosities of the copolymer solutions. However, from the pictures, it can be infered that, in the range of temperatures investigated, it was not verified a significant change on the reduced viscosities of the copolymers. Interestingly, they showed a behaviour similar from that of polyacrylamide [1, 20], whereas the reduced viscosities were essentially constant within the range of temperatures investigated.

In Figures 1 and 2 it is also observed that, all over the temperatures studied, the copolymer 5 shows higher reduced viscosity values compared to copolymer 4. This behaviour is due to the greatest molecular weight of copolymer 5 which leads to a larger hydrodynamic volume and consequently, an increase of the reduced viscosity. Additionally, on semi-dilute region, an influence of the chain structure is expected and as the hydrophobe chain length increases from 400 to 1000, the reduced viscosity of the solution becomes higher, owing to the effect of intermolecular associations. Thus, it is important to note that the effect of the hydrophobic groups depends on polymer concentration.

CONCLUSIONS

In summary, we can conclude that associating polymer rheology can be affected by hydrophobe type and content, besides molecular weight, polymer concentration and presence of salts. Moreover, the addition of ionic substances (NaCl) to the polymer solution has an effect of reducing the hydrodynamic volume of the polymer molecule as a result of intrachain association due to the water-structuring effect of NaCl. Thence, it was observed the smaller intrinsic viscosities for the polymers with more graft chain contents, since the latter show an increase in the number of interactions.

No substantial effect of temperature on the reduced viscosity of the solution, at the range investigated, was achieved. However, complete study of the influence of temperature on these copolymers has yet to be achieved and so, further work in this domain is still required.

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