

Influence of Surfactant and Salt Concentration on the Rheological Properties of Three Different Microstructures of Associative Polyelectrolytes Obtained by Solution Polymerization

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Abstract

The rheological properties of three different microstructures of hydrophobically modified alkali-soluble polymers (telechelic, multisticker and combined) in the presence of various concentrations of anionic surfactant and salt (NaCl) were investigated. Associative polymers containing both ionic sites and small number of hydrophobic groups were obtained, and their thickening properties in aqueous solutions, were investigated. Solution polymerization was used for obtaining the different polymers. Relationships between hydrophobe, sodium dodecyl sulfate (SDS) and NaCl concentration are proposed. Owing to the competition between attractive hydrophobic interaction and repulsive electrostatic interactions, such hydrophobically modified polymers exhibit various rheological behaviors in aqueous solutions, depending on microstructure of polyelectrolyte, SDS and NaCl concentrations.

Keywords

Polymerization, Associative Polyelectrolyte, Rheology, Surfactant and Salt Concentration

1. Introduction

The great amount of applications of water-soluble polymers at industrial level (paints and coatings, cosmetology,

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paper industry, biomedical applications, etc.). [1]-[5] had attracted great interest of study on other synthesis methods to achieve improvements in the rheological properties of polymer. Since then, several studies have been carried out to disclose rheological behavior of polymers and increase their thickening capacity; studies to increase solution viscosity range from molecular weight grow, use of polyelectrolytes, up to emergence of associative polymers. Associative polymers are hydrophilic chains that contain hydrophobic groups in the chain ends (telechelic polymers) [6]-[8], or distributed along polymeric chain (multisticker polymers) [9]-[11]. In aqueous solution, hydrophobic groups interact in an intra- and inter-molecular way forming three-dimension networks, therefore increasing solution viscosity. Recently, Jiménez *et al.* developed a polymer that has hydrophobic groups as well as in chain ends as within hydrophilic chain section which is called combined polymer [12]-[14], that has good thickening properties due to network-type structures they develop.

Associative polymers can synthesize by several polymerization techniques. There are different kinds of associative polymers, being hydrophobically modified alkali-soluble emulsion polymers (HASE) [15]-[17] the most used, that have the advantage of significantly increasing solution viscosity at very low concentrations. Nevertheless, in studies carried out there have been problems with emulsion stabilization, therefore telechelic or combined type structures cannot be obtained due to stabilization issues of final latex. This disadvantage in the process by emulsion, leads to search for other polymerization techniques, and among them, can be listed polymerization in solution, in which there are no stabilization issues and it is possible to obtain telechelic and combined type polymers without stabilization problems of polymerization in emulsion.

In this work the aim is to study different polymeric structures (telechelic, multisticker and combined type) synthesized by polymerization in solution at different polymer concentrations. It is proposed to use same monomers as for HASE polymers synthesis (methacrylic acid, ethyl acrylate, hydrophobic macromonomer) and hydrophobic initiator. Also, a rheological study was carried out in order to determine influence of the surfactant sodium dodecylsulfate, SDS, and sodium chloride, NaCl, salt on rheological properties of polymeric solutions.

2. Experimental

Synthesis of Hydrophobic Initiator ACVA₁₆. The hydrophobic initiator was synthesized according to the method reported by Pérez *et al.* [18], which consists of functionalizing the azoic acid 4,4-azobiscyanovaleric acid (ACVA) with an esterification reaction between ACVA and hexadecanol, giving as result the lineal hydrophobic initiator ACVA₁₆. Yield of 85% was achieved, which was determined by gravimetric analysis.

Synthesis of Lineal Hydrophobic Monomer Hexadecanyl Acrylate (MH16). The synthesis of hydrophobic monomer hexadecanyl acrylate (MH16) was carried out according to the method reported by Valint *et al.* [19]; it starts with replacement reaction between acryloyl chloride and hexadecanol. Triethylamine is used as receptor of HCl that is produced during reaction. The obtained yield was of 29%, which was determined by gravimetry.

Polyelectrolytes Synthesis. Polyelectrolytes synthesis was made with different structures, including the reference polyelectrolyte without hydrophobic groups. AMA, AE, and MH₁₆ were the monomers used. All polyelectrolytes were synthesized at a 70% in weight concentration in solids. The procedure is described as follows: in 100 mL reactor prepared with mechanical stirring and reflux it is added the initial defined quantities of AMA, AE, MH₁₆ and ethanol (saving an amount of the latter to dissolve the initiator ACVA or ACVA₁₆). It is applied degassing with nitrogen during 30 minutes. Temperature is increased to 70°C. It is added the quantity of initiator dissolved in ethanol and polymerization starts during a 3 hours period. Once reaction is finished, it is added THF to reactor to dissolve polymer and then it is precipitated in hexane. Finally, the polymer is dried under vacuum 50°C. The quantities used in each synthesis reaction for different electrolytes are listed in **Table 1**.

2.1. Rheological Study

The rheological study was performed on a Paar Physica UDS 200 rheometer coupled to a Julabo F 25 heating bath. It was used cone-plate geometry (50 mm ²). The study was made under steady state at temperature of 25°C ± 0.04°C and an interval of shear rate measurements from 0.01 to 1000 s⁻¹.

2.2. Preparation of Samples for Rheological Study

Preparation of Samples in Water. The samples were prepared weighing defined quantities of polymer (1, 1.5 and 2% in weight) and dissolving them in deionized water. In order to make possible the dissolving, the samples were neutralized at a pH of approximately 9 adding drop by drop an AMP (2-amino-2-methyl-1-propanol) at

Table 1. Concentration of reagents for the synthesis of polyelectrolytes.

Reactive	Polymer	Reference (R-70)		Telechelic (T-70)		Multisticker (M-70)		Combined (C-70)	
		mol	g	mol	g	mol	g	mol	g
	AMA	0.188	16.18	0.188	16.18	0.1698	14.61	0.169	14.61
	AE	0.188	18.82	0.188	18.82	0.1698	16.99	0.169	16.99
	MH ₁₆	---	---	---	---	0.0141	4.17	0.014	4.17
	ACVA ₁₆	---	---	0.0012	0.91	---	---	0.0012	0.91
	ACVA	0.001	0.35	---	---	0.00125	0.91	---	---
	Ethanol	0.325	15	0.325	15	0.3256	15	0.325	15

99% solution. During a 24 hours period samples were kept under stirring.

Preparation of Samples with SDS or NaCl. At each solution of the previously prepared ones, it was added the required amount of SDS or NaCl to achieve the desired concentrations, during 24 hours these solutions were stirred and dilutions corresponding to each structure were made with them.

Preparation of samples with SDS and NaCl. In order to prepare the samples, it was used each prepared solution with water and it was added the required amount of SDS to achieve the greatest concentration (3, 10 or 15 mM according the structure of each polymer), this solution was stirred during 24 hours and it was used to make the dilutions corresponding to each structure. During 24 hours solutions were stirred. At each polymer/surfactant solution different NaCl concentrations there were added, and during 24 hours solutions were stirred.

3. Results and Discussions

3.1. Synthesis of Polyelectrolytes

Table 2 lists conversions obtained for each one of polymers.

3.2. Rheological Study

3.2.1. Study of Polyelectrolytes with SDS

In **Figure 1** is shown the variation of the zero-shear viscosity (η_0) in function of SDS concentration (C_{SDS}), of different associative polyelectrolytes at a polymer concentration (C) of 2 wt%. For the case of reference polyelectrolyte (R-70), there is no variation in measured viscosity as long as SDS quantity is increased, this is expected due this polymer has no hydrophobic groups that could create changes in viscosity with SDS. For the case of telechelic type polyelectrolyte (T-70) it is detected an increase in viscosity up to concentration of 1 mM of SDS, followed by a decrease, this behavior is typical of associative polymers and it has been previously observed [20]. For multisticker polymer (M-70) and combined polymer (C-70) it is observed also an increase in viscosity as long as SDS concentration increases, but these polymers do not have this peak, which could arise at greater SDS concentrations.

Telechelic Polyelectrolytes. **Figure 2** shows η_0 variation in function of C_{SDS} for polymer T-70 at different polymer concentrations. A slight increase of viscosity is detected as long as surfactant is added. The reason of this increase is because surfactant strengthens system's intra-molecular and inter-molecular interactions, because when adding SDS molecules they introduce themselves on hydrophobic groups, causing that bonding time on hydrophobic groups becomes longer. Other possible reason could be that surfactant favors formation of new hydrophobic bonds. After this peak, a decrease in viscosity is observed, because surfactant solubilizes the hydrophobic parts, breaking the bonds.

Multisticker Polyelectrolytes. **Figure 3** shows η_0 variation in function of C_{SDS} for polymer M-70 at different polymer concentrations. It is observed that for samples at 1 wt%, it is seen a decrease of viscosity with a concentration of 2 mM of SDS and it practically stays the same when increasing SDS. It is also noted that viscosity values are bellow when compared to samples without SDS, this behavior is because at this polymer concentration there are not enough hydrophobic groups that allow to detect any viscosity variation. For samples of 1.5 and 2 wt%, it is observed a constant increase in viscosity without reaching a peak; this because surfactant concentration is not enough to solubilize each hydrophobic group and is not seen a decrease in viscosity.

Table 2. Conversion of polyelectrolytes.

Polymer	Conversion (wt%)
R-70	94.7
T-70	63.4
M-70	88.4
C-70	86.5

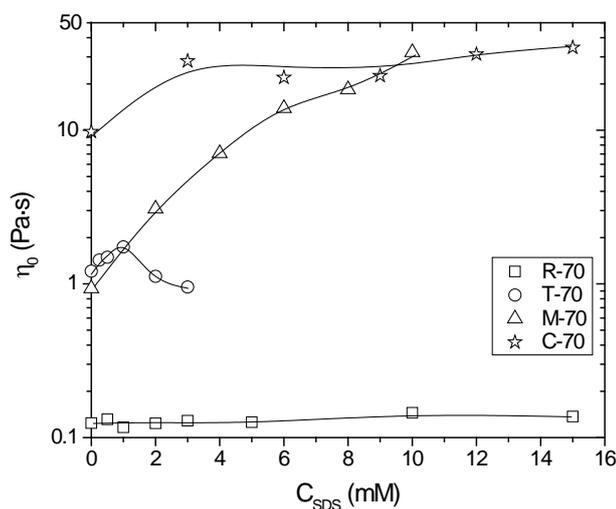


Figure 1. Viscosity (η_0) in function of SDS concentration (C_{SDS}), of different associative polyelectrolytes at a polymer concentration (C) of 2 wt%.

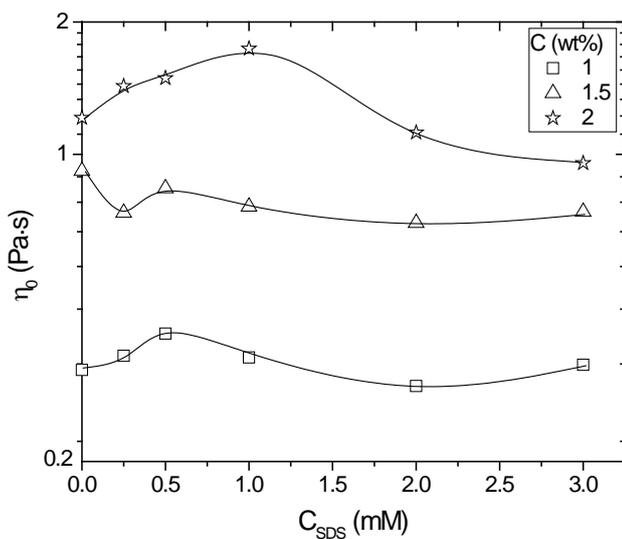


Figure 2. Variation of η_0 in function of C_{SDS} for polymer T-70 at different polymer concentrations.

Combined Polyelectrolytes. Figure 4 shows η_0 variation in function of C_{SDS} for polymer C-70a at different polymer concentrations. It shows typical bell-type curve behavior in samples at 1 and 1.5 wt% with a maximum at 6 mM of SDS. For sample at 2 wt%, it is observed an increase in viscosity up to a concentration of 3 mM of SDS followed by a slight decrease at 6 and 9 mM of SDS. At 12 and 15 mM of SDS it is observed a slight increase, this because at this concentration (2 wt%) the amount of hydrophobic groups is enough so the quantity of

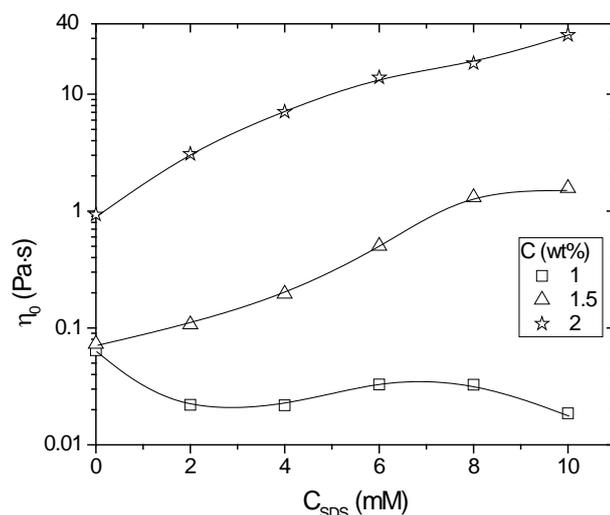


Figure 3. Variation of η_0 in function of C_{SDS} for polymer M-70 at different polymer concentrations.

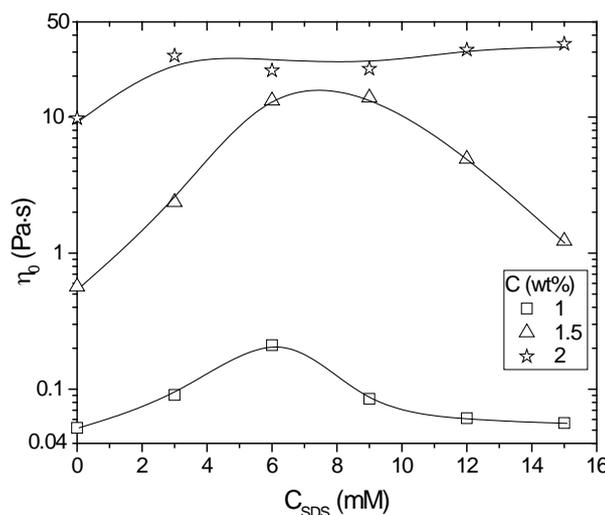


Figure 4. Variation of η_0 in function of C_{SDS} for polymer C-70 at different polymer concentrations.

SDS cannot solubilize the hydrophobic parts and there is no peak, therefore this peak is under greater concentrations of SDS than the ones studied in this work.

3.2.2. Study of Polyelectrolytes with NaCl

In **Figure 5** is shown η_0 variation in function of NaCl concentration (C_{NaCl}) of different associative polyelectrolytes at polymer concentration (C) of 2 wt%. For polymers R-70 and T-70, it is observed a remarkable decrease in viscosity, this because presence of salt breaks electrostatic repulsions, which causes that polymer chains retract, diminishing hydrodynamic volume and therefore system viscosity, for the case of T-70 they contain very few hydrophobic groups (only two per chain), then by this reason they do not impede breaking of electrostatic repulsions. For the case of M-70, it is observed a peak in viscosity, this could be explained as in the case of interactions associative polymer/surfactant, in the extent that NaCl is added, this introduces hydrophobic parts causing an increase of viscosity, when they are saturated by salt, moving this salt to the reaction media and breaking electrostatic repulsions, and therefore showing a decrease of viscosity. For the case of C-70 polymer there is no viscosity variation with respect C_{NaCl} and this probably is due high amount of hydrophobic groups that not allow to distribute salt in the media.

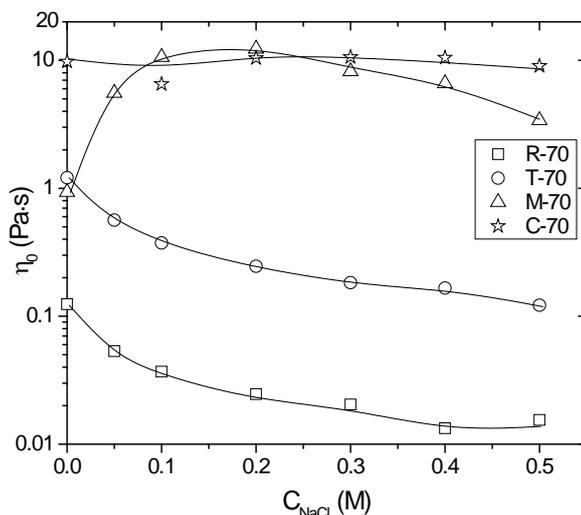


Figure 5. Variation of η_0 in function of NaCl concentration (C_{NaCl}) of different associative polyelectrolytes at polymer concentration (C) of 2 wt%.

Telechelic Polyelectrolytes. Figure 6 shows η_0 variation in function of C_{NaCl} for T-70 at different concentrations of polymer. It is observed a decrease in viscosity with salt for all studied polymer concentrations. As it was previously mentioned, this can be attributed to the fact that there is little amount of hydrophobic groups (only two hydrophobic groups per chain), therefore most of salt goes to aqueous phase and, as in the case of polymer R-70, breaks electrostatic repulsions giving as result a decrease in viscosity.

Multisticker Polyelectrolytes. Figure 7 shows η_0 variation in function of C_{NaCl} for M-70 at different concentrations of polymer. For sample at 1 wt%, it is observed a decrease in viscosity when increasing salt concentration, as observed in study of concentration of SDS for same polymer (Figure 3). Also at this concentration (1 wt%) polymer viscosity as well with SDS as with NaCl is lower than polymer without additives (SDS or NaCl). Considering that salt acts like SDS, in other words, is led towards hydrophobic sections and reinforces them, it could result that once they are saturated, the salt goes to the media (water) generating break of electrostatic repulsions and therefore diminishes viscosity. This behavior can be explained just like the case of SDS previously mentioned, that at this concentration the amount of hydrophobic groups is so small and most part of salt goes to water. On the other hand, samples at 1.5 and 2 wt% have a peak in viscosity at a concentration of 0.2 M of NaCl. This could be because there are more hydrophobic groups in the media and salt is introducing into them and acts like surfactant, allowing creation of new bonds or increasing time that system's intermolecular bonds last. The decrease in viscosity could be due with increase in salt concentration, the hydrophobic groups are saturated with salt and this goes to water breaking electrostatic repulsions, polymer chains begin to contract and also it is possible that intermolecular hydrophobic bonds break.

Combined Polyelectrolytes. Figure 8 shows η_0 variation in function of C_{NaCl} for polymer C-70 at different concentrations of polymer. For samples at 1 and 1.5 wt%, it is shown an increase in viscosity when increasing salt concentration up to a level where viscosity stabilizes. This behavior is because, as previously mentioned, salt acts as surfactant that can favor creation of new bonds or reinforce them. For sample at 2wt%, such increase is not detected, but there is a constant behavior in viscosity at different salt concentrations.

3.2.3. Study of Polyelectrolytes with SDS and NaCl

Telechelic Polyelectrolytes. In Figure 9 is shown η_0 variation in function of C_{NaCl} for polymer T-70a at 1 wt% for different SDS concentrations. In all series of samples at different surfactant concentration is observed a decrease in viscosity, following the trend of this same polymer at different concentrations of NaCl and SDS separately. There is observed only a slight increase in viscosity due effect given by SDS of reinforcing bonds of hydrophobic groups, however the values are very low. For concentrations in polymer of 1.5 and 2% they show the same behavior previously mentioned.

Multisticker Polyelectrolytes. In Figure 10 is shown η_0 variation in function of C_{NaCl} for polymer M-70 at 1

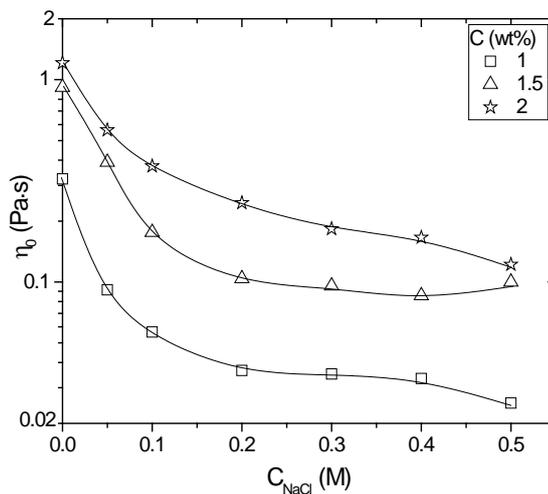


Figure 6. Variation of η_0 in function of C_{NaCl} for T-70 at different concentrations of polymer.

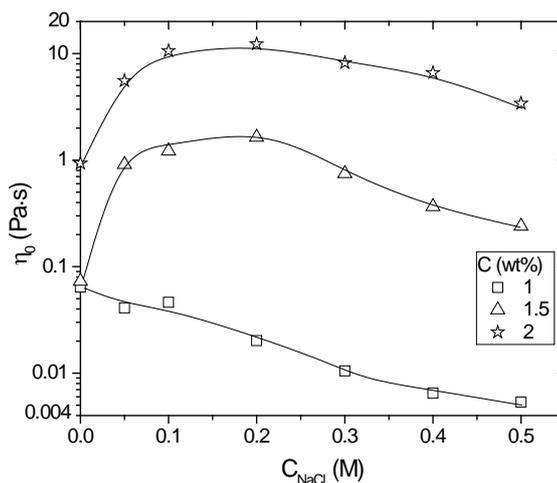


Figure 7. Variation of η_0 in function of C_{NaCl} for M-70 at different concentrations of polymer.

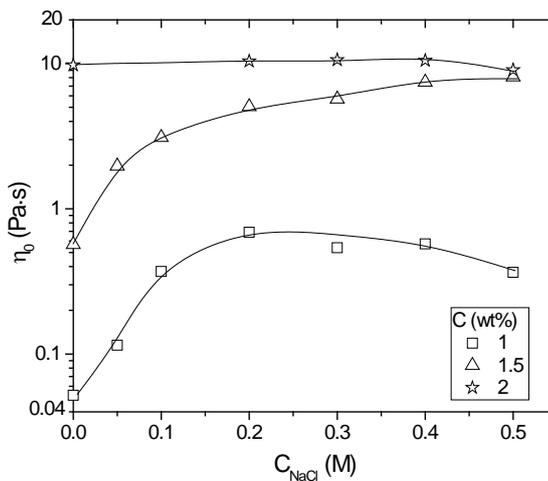


Figure 8. Variation of η_0 in function of C_{NaCl} for C-70 at different concentrations of polymer.

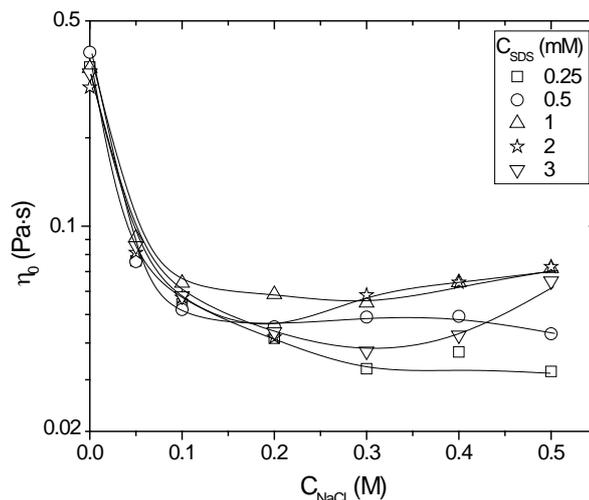


Figure 9. Variation of η_0 in function of C_{NaCl} for polymer T-70a at 1 wt% for different SDS concentrations.

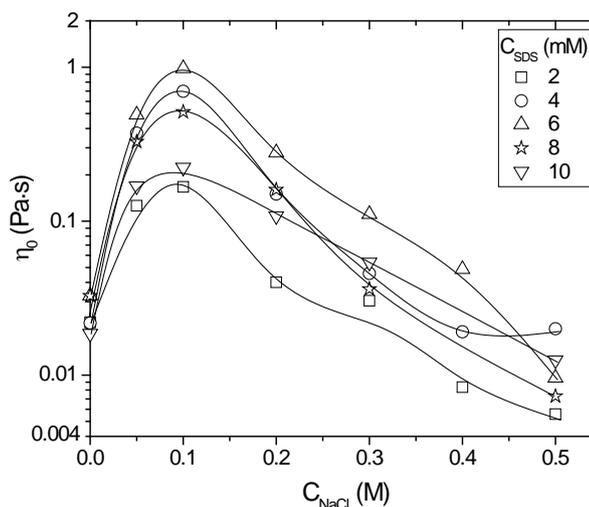


Figure 10. Variation of η_0 in function of C_{NaCl} for polymer M-70a at 1 wt% for different SDS concentrations.

wt% for different SDS concentrations. Despite that in the independent study with SDS or salt for this polymer at 1% in weight they show a decrease in viscosity, in the study with SDS and NaCl, is set a peak in viscosity at 0.1 M of NaCl, which can be due to a combined effect of strengthening to hydrophobic groups by SDS and NaCl, potential new bonds or an increase in duration of such bonds. For samples at 1.5 and 2 wt% it is observed the same result, showing a peak at 0.1 M of NaCl in all cases.

Combined Polyelectrolytes. In **Figure 11** is shown η_0 variation in function of C_{NaCl} for polymer C-70 at 1 wt% for different SDS concentrations. In all cases it is observed an increase in viscosity with NaCl concentration and the behavior showed for each series coincides with behavior of studies performed aside for SDS and NaCl. The viscosity is increased at least in 1 order of magnitude with respect the ones obtained adding SDS and NaCl independently; this can be explained by the fact that salt strengthens bonds of hydrophobic groups already strengthened with SDS, also could be due an increase in the number of intermolecular associations. The polymer has the same behavior (increase in viscosity with C_{NaCl}) for samples at 1.5 and 2 wt%.

4. Conclusions

Associative polyelectrolytes synthesis was achieved via free radical polymerizations in solution obtaining three

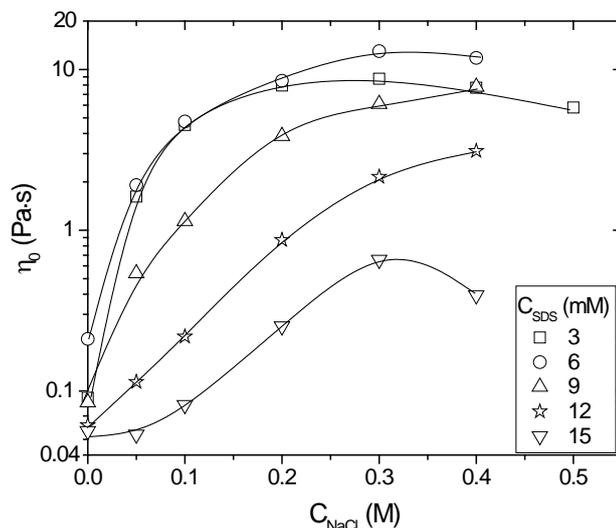


Figure 11. Variation of η_0 in function of C_{NaCl} for polymer C-70a at 1 wt% for different SDS concentrations.

different microstructures (telechelic, multisticker and combined) at a concentration of 70 wt% solids. Polyelectrolytes that provided higher viscosity in aqueous solution were of the combined type, followed by multisticker and telechelic type in that order. The SDS has a significant influence on the thickening properties of polyelectrolytes, providing a further increase in viscosity at a certain surfactant concentration. The surfactant structure showed a great influence in the increase in viscosity, the greater being the combined, followed by multisticker and to a lesser extent telechelic. The study shows that the effect of NaCl in the combined and multisticker structures, shows a significant increase in viscosity, however the telechelic polyelectrolytes show a decrease in viscosity with increasing salt concentration. For multisticker and combined structures good thickening properties are presented by the combined effect of SDS and NaCl, where high viscosities are attained.

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