# Characterization of Polyelectrolyte Effect in Poly(Acrylic Acid) Solutions

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**ABSTRACT:** The viscometric behavior of poly(acrylic acid) solutions, as well as their ion transport properties, were monitored as a function of polymer concentration and the addition of KOH in nonisoionic conditions. Polyelectrolyte effect was studied and characterized by conductivimetry as well as viscometric properties at the infinite dilution limit. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 191–196, 2003

**Key words:** poly(acrylic acid); neutralization; polyelectrolyte effect

## INTRODUCTION

Polyelectrolytes comprise a class of macromolecules which, in our daily life, has an importance of its own. In the biomedical field, they are widely used in many systems, such as dental adhesives and restorations, controlled release devices, and biocompatible materials[1]; in the coating industry as well in the pharmaceutical industry, they are intensively used as thickeners.[2,3] Because of their tendency to adsorb onto solid surfaces, they are employed in their modification through the application of polyelectrolyte-based coatings and adhesives[4,5]; in the case of water treatment, they are largely used as flocculants.[6]

Regarding its use as a thickener, it has been shown that to deal with the rheology of poly(acrylic acid) solutions, it is very important to understand the behavior of this polymer (as well as its related copolymers) in dilute solutions; the relationship between degree of neutralization, intra-, and intermolecular interactions must be reasonably established, the approach often used in this case being (experimental and theoretically) the isoionic dilution method.[7–11] When using this class of polymers to stabilize alumina dispersions by adsorption, polymer conformation also plays an important role: at high ionic strength conditions (high salt concentration), macromolecular dimensions are smaller, making adsorption more probable.[12]

All these facts make polyelectrolytes per se to represent an academically very interesting subject, as one can find in the literature. Kazakov et al. have used light scattering to study the effect of poly(acrylic acid) conformation on the properties of polymer–protein conjugates.[13] Yin et al. studied the swelling of this class of polymers jointly with their biodegradation in controlled drug-release systems.[14] Nasredinne et al. studied the conformation of acrylic acid based copolymers using NMR and FTIR spectroscopy.[15] In the specific case of this work, we will study the polyelectrolyte effect in poly(acrylic acid) solutions as a function of the addition of the neutralizing agent KOH. This will be done by the determination of reduced viscosity and conductivity as a function of polymer concentration at different KOH/COOH ratios without the isoionic approach to the problem.

## EXPERIMENTAL

Poly(acrylic acid) of $\bar{M}_w \approx 2.5 \times 10^5$ and $1.25 \times 10^6$ g/mol, here named PAA-250 and PAA-1250, respectively, were purchased from Aldrich (Milwaukee, WI) and used as received. The solutions were obtained by mixing a given amount of polymer (weighted in a dried basis) with water and KOH (Synth, Brazil), at different $n_{KOH}/n_{COOH}$ ratios. The solutions were kept under stirring for 24 h prior to any measurement [constant values of viscosity and conductivity after the first day were taken as indications that the solution reached equilibrium, concerning the solubilization of the poly(acrylic acid)].

Viscometry was carried out by using a Cannon–Fenske viscometer 100, previously calibrated with different fluids. The flow time in these measurements was never lower than 100 s. Reduced viscosity, $\eta_{red}$, was calculated according to eq. (1)[16]:
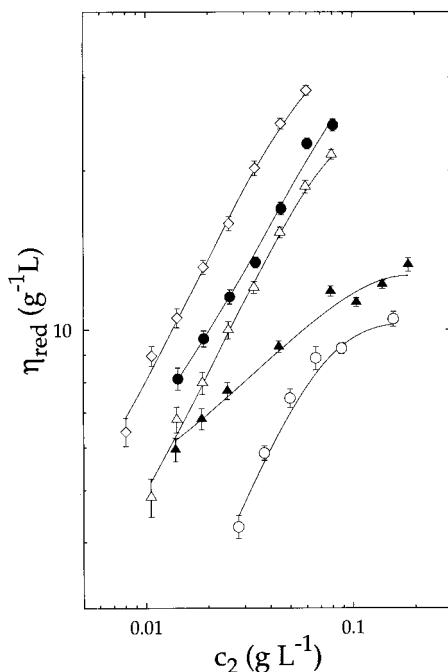
**Figure 1** Reduced viscosity ($\eta_{red}$) as a function of polymer concentration ($c_2$) for poly(acrylic acid), $\bar{M}_v = 1.25 \times 10^6$ g/mol (PAA-1250) for different KOH to COOH molar ratios ($n_{KOH}/n_{COOH}$). White circles: $n_{KOH}/n_{COOH} = 0$. White triangles: $n_{KOH}/n_{COOH} = 0.3$. White diamonds: $n_{KOH}/n_{COOH} = 0.45$. Filled circles: $n_{KOH}/n_{COOH} = 0.75$. Filled triangles: $n_{KOH}/n_{COOH} = 1$. The continuous lines represent eq. (3).

$$\eta_{red} = \frac{1}{c_2}\left(\frac{t}{t_0} - 1\right) \tag{1}$$

where $t_0$ is the flow time of the solvent and $t$ is the flow time of a given polymer solution with mass/volume concentration of $c_2$.

Conductivimetry was carried out by using a Digimed conductivimeter, model DM31, with a cell consisting of two parallel plates covered with platinum with a conductivimeter cell constant, $k = 0.1$ cm$^{-1}$, and current frequency, $\omega = 1$ kHz.

## RESULTS AND DISCUSSION

Figure 1 shows plots of reduced viscosity as a function of polymer concentration, $c_2$, for PAA-1250. When working with this specific molecular weight, we used the following $n_{KOH}/n_{COOH}$ ratios: 0, 0.3, 0.45, 0.75, and 1. Higher ratios resulted in quite scattered values of flow time (especially at higher concentrations). One can see that, differently from the behavior predicted by the Flory–Huggins relationship, there is a deviation to lower values of $\eta_{red}$ as the values of $c_2$ increase. According to the treatment given by Antonietti et al., $\eta_{red}$ can be written as the result of the addition of effects of electrostatic long range interactions[17]:

$$\eta_{red} = [\eta](1 + k_1[\eta]c_2) + \eta_{red,lr} \tag{2}$$

where $\eta_{red,lr}$ represents the increase of reduced viscosity due to electrostatic long-range interactions. There are two main reasons for the increase in $\eta_{red,lr}$: the ionization of polymer groups along the chain and, regarding the isoionic conditions, the decrease in low molecular weight electrolyte concentration, a situation which has an interesting theoretical approach developed by Hess and Klein.[18] Consequently, in the case of the present work, negative deviations of a linear relationship between $\eta_{red}$ and $c_2$ may be attributed to a decrease in the values of $\eta_{red,lr}$ as concentration increases. Because poly(acrylic acid) is a weak polyacid, its degree of dissociation decreases as concentration increases, so that long-range interactions due to electrostatic repulsion are disfavored, resulting in polymer chains with smaller volumes.

One can see that, in the range of concentrations studied, as $n_{KOH}/n_{COOH}$ increases, $\eta_{red}$ increases, reaching a maximum at $n_{KOH}/n_{COOH} \approx 0.45$. From this point, the deviation to lower values of $\eta_{red}$ becomes more pronounced, resulting in a behavior very similar to the poly(acrylic acid) without any neutralization. One reason for this behavior is that when increasing the $n_{KOH}/n_{COOH}$ ratio, there is an increase in neutralization of carboxyl groups; however, Konop and Colby have shown that, when using NaOH as the alkali, just a fraction of the carboxyls are effectively charged[19] and, because poly(acrylic acid) is a weak polyacid, one would expect a certain amount of Na$^+$ and OH$^-$ free ions in solution. As a consequence, a maximum value of $\eta_{red}$ would be the result of the superposition of two opposite contributions to the reduced viscosity: the increase in neutralization would lead to an increase in viscosity because of negative-charge repulsion and the increase in the concentration of low molecular weight electrolyte would lead to a decrease in viscosity, because of the shielding effect of K$^+$ and OH$^-$ ions on the same charges, decreasing the repulsive force between them and, as a consequence, macromolecular volume and $\eta_{red}$.[11] In the specific case of PAA-1250, the dependence of $\eta_{red}$ in relation to $c_2$ was given by the following empirical relationship:

$$\ln \eta_{red} = \ln[\eta] + a_0 c_2 e^{-a_1\sqrt{c_2}} \tag{3}$$

where $[\eta]$ is the intrinsic viscosity, and $a_0$ and $a_1$ are constants. This equation was used to estimate the values of intrinsic viscosity, which are analyzed at the end of this section.
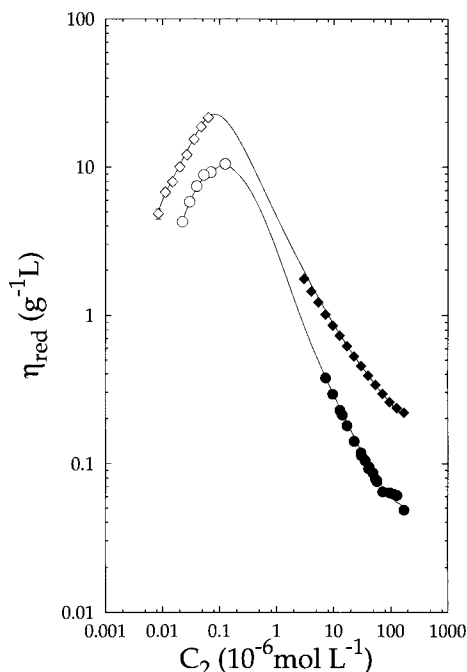
We used the experiments with PAA-250 to analyze the behavior of the solutions at higher $n_{KOH}/n_{COOH}$ ratios (Fig. 2): in the case of this polymer, the resultant solutions did not yield scattered flow times, so that it
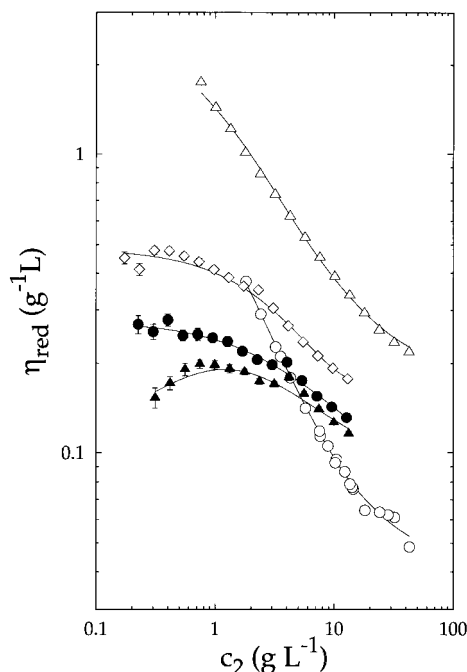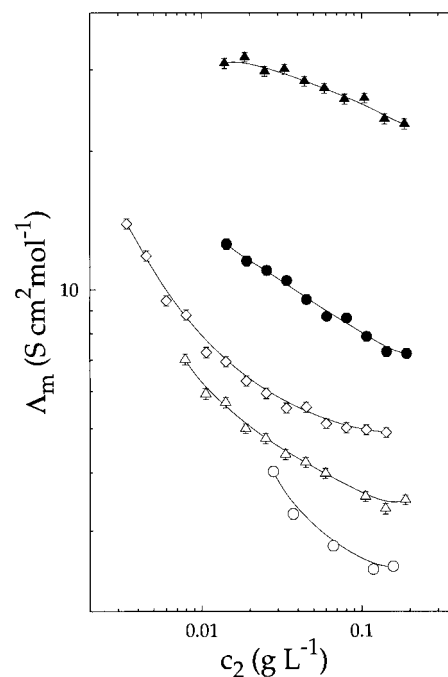
**Figure 2** Reduced viscosity ($\eta_{red}$) as a function of polymer concentration ($c_2$) for poly(acrylic acid), $\bar{M}_v = 2.5 \times 10^5$ g/mol (PAA-250) for different KOH to COOH molar ratios ($n_{KOH}/n_{COOH}$). White circles: $n_{KOH}/n_{COOH} = 0$. White triangles: $n_{KOH}/n_{COOH} = 0.3$. White diamonds: $n_{KOH}/n_{COOH} = 1.1$. Filled circles: $n_{KOH}/n_{COOH} = 2$. Filled triangles: $n_{KOH}/n_{COOH} = 2.4$.



**Figure 3** Reduced viscosity ($\eta_{red}$) as a function of molar polymer concentration ($c_2$) for poly(acrylic acid). Open circles: PAA-1250 ($\bar{M}_v = 1.25 \times 10^6$ g/mol) with $n_{KOH}/n_{COOH} = 0$. Filled circles: PAA-250 ($\bar{M}_v = 2.5 \times 10^5$ g/mol) with $n_{KOH}/n_{COOH} = 0$. Open diamonds: PAA-1250 ($\bar{M}_v = 1.25 \times 10^6$ g/mol) with $n_{KOH}/n_{COOH} = 0.3$. Filled diamonds: PAA-1250 ($\bar{M}_v = 2.5 \times 10^5$ g/mol) with $n_{KOH}/n_{COOH} = 0.3$.

was possible to carry out measurements at high $n_{KOH}/n_{COOH}$ ratios (we used the following ratios in this study: 0, 0.3, 1.1, 2, and 2.4). There also is an increase in values of $\eta_{red}$, as $n_{KOH}/n_{COOH}$ increases, up to a maximum, as in the specific case of PAA-1250, but now at $n_{KOH}/n_{COOH} \approx 0.3$. On the other hand, if one analyzes Figure 2, one can see that, when working with these solutions, the kind of mathematical relationship expressed by eq. (3) seems to be useless, because there are no points to estimate [$\eta$] because $\eta_{red}$ continuously falls with increasing $c_2$, apart from the case in which $n_{KOH}/n_{COOH} = 2.4$. In this case, one can observe a curve with the same shape as the obtained by Roure et al. in the case of sodium polystyrene sulfonate solutions in the presence of low salt concentration.[20] In our case, although KOH is an alkali, it could play the same rule (in an electrostatic sense) when in excess.

One can also see that, apart from the case in which $n_{KOH}/n_{COOH} = 2.4$, all the curves fall down for PAA-250, while they seem to go to a maximum, in the case of PAA-1250. That could be explained by the approach used by Nishida et al. when developing a theoretical model for analyzing the behavior of polyelectrolyte solutions.[21] Starting from the point that electrostatic interactions would be responsible for increasing viscosity, the mentioned authors divided this influence into intra- and intermolecular components:



**Figure 4** Molar conductivity ($\Lambda_m$, per mole of mer) as a function of polymer concentration ($c_2$) for poly(acrylic acid), $\bar{M}_v = 1.25 \times 10^6$ g/mol (PAA-1250) for different KOH to COOH molar ratios ($n_{KOH}/n_{COOH}$). White circles: $n_{KOH}/n_{COOH} = 0$. White triangles: $n_{KOH}/n_{COOH} = 0.3$. White diamonds: $n_{KOH}/n_{COOH} = 0.45$. Filled circles: $n_{KOH}/n_{COOH} = 0.75$. Filled triangles: $n_{KOH}/n_{COOH} = 1$.
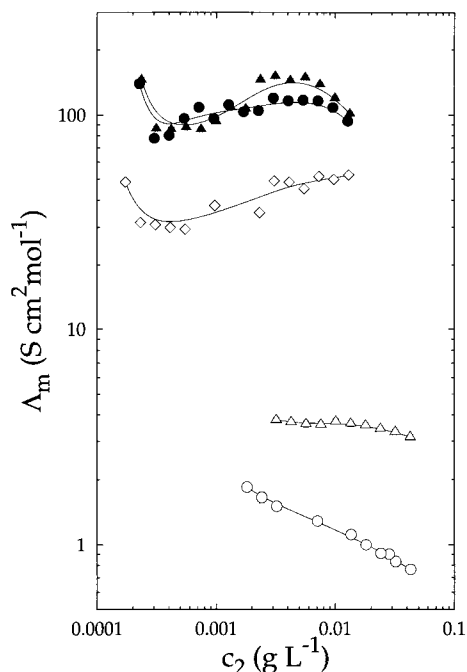
**Figure 5** Molar conductivity ($\Lambda_m$, per mole of mer) as a function of polymer concentration ($c_2$) for poly(acrylic acid), $\bar{M}_v = 2.5 \times 10^5$ g/mol (PAA-250) for different KOH to COOH molar ratios ($n_{KOH}/n_{COOH}$). White circles: $n_{KOH}/n_{COOH} = 0$. White triangles: $n_{KOH}/n_{COOH} = 0.3$. White diamonds: $n_{KOH}/n_{COOH} = 1.1$. Filled circles: $n_{KOH}/n_{COOH} = 2$. Filled triangles: $n_{KOH}/n_{COOH} = 2.4$.

$$\eta_{red} = \eta_{red,intramolecular} + \eta_{red,intermolecular} \qquad (4)$$

According to the authors, the second term is related to the expression developed by Rice and Kirkwood, for the contribution of intermolecular potential to the solution viscosity,[22] and is the main cause for the presence of the maximum which appears in Figure 2, $n_{KOH}/n_{COOH} = 2.4$. Still, according to their model, these maxima are located at a polymer concentration from $10^{-4}$ to $10^{-3}$ mol/L. It seems that, because of its higher molecular weight, the range of concentration used for PAA-1250 was before the maximum, while the range used for PAA-250 was after the maximum. To strengthen this hypothesis, in Figure 3 we plotted reduced viscosity against estimated molar polymer concentration (using $\bar{M}_v$ nominal values) for PAA-250 and PAA-1250 with $n_{KOH}/n_{COOH} = 0$ and 0.3. One can see that, in both cases, we have a maximum around $10^{-7}$ mol/L, which is not in the range cited before but qualitatively reproduces the expected behavior.

Figures 4 and 5 depict the relationship between molar conductivity (in terms of mer mole) and the concentration of polymer for PAA-1250 and PAA-250, respectively. For any weak electrolyte, molar conductivity decreases with concentration; in fact, for a weak monoprotic acid, the degree of dissociation is inversely proportional to the square root of its concen-

tration, implying that an increase in concentration results in the decrease of molar conductivity.[23] One can observe the decrease in molar conductivity, certainly due to this decrease in dissociation in both figures, except from the data with $n_{KOH}/n_{COOH} > 1$ (Fig. 5). When this ratio is higher than 1, if one increases polyelectrolyte concentration, polyacid dissociation decreases; on the other hand, the concentration of the strong electrolyte KOH increases, resulting in an increase in molar conductivity (as defined here: the conductivity divided by mer molar concentration). The result of the balance between the increase in KOH concentration and decrease in COO$^-$ concentration will establish if the molar conductivity will rise or fall. Finally, one can see that for higher amounts of KOH, the conductivity rises and then decreases, certainly due to shocks between ions which obstruct ion transport within the solution.

Because all the experiments carried out were not performed in isoionic conditions, at first sight one should expect to be unfeasible to carry out a hydrodynamic approach to the study, mainly through the analysis of Huggins constant $k_1$, which is related to the intrinsic viscosity [$\eta$] and reduced viscosity $\eta_{red}$ as[24]

$$\eta_{red} = [\eta] + k_1[\eta]^2 c_2 \qquad (5)$$

We saw that $\ln[\eta]$ can be calculated (only in the case of PAA-1250) by using eq. (3). Having in mind that, for a weak electrolyte, when the concentration tends to
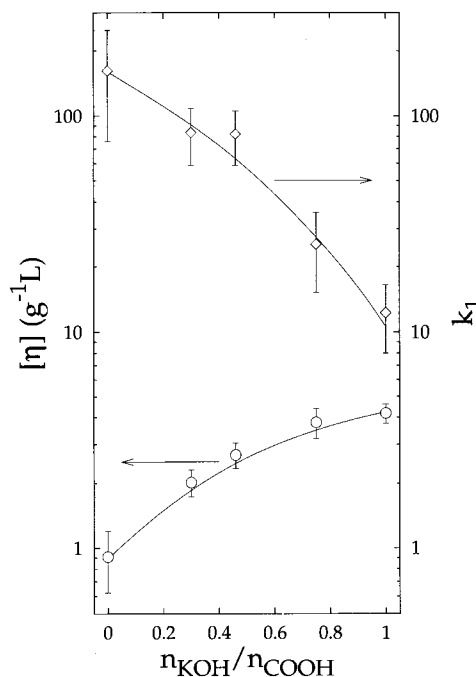


**Figure 6** Intrinsic viscosity ([$\eta$], white circles) and Huggins constant ($k_1$, white diamonds) as a function of KOH to COOH ratio ($n_{KOH}/n_{COOH}$) for poly(acrylic acid) $\bar{M}_v = 1.25 \times 10^6$ g/mol (PAA-1250).
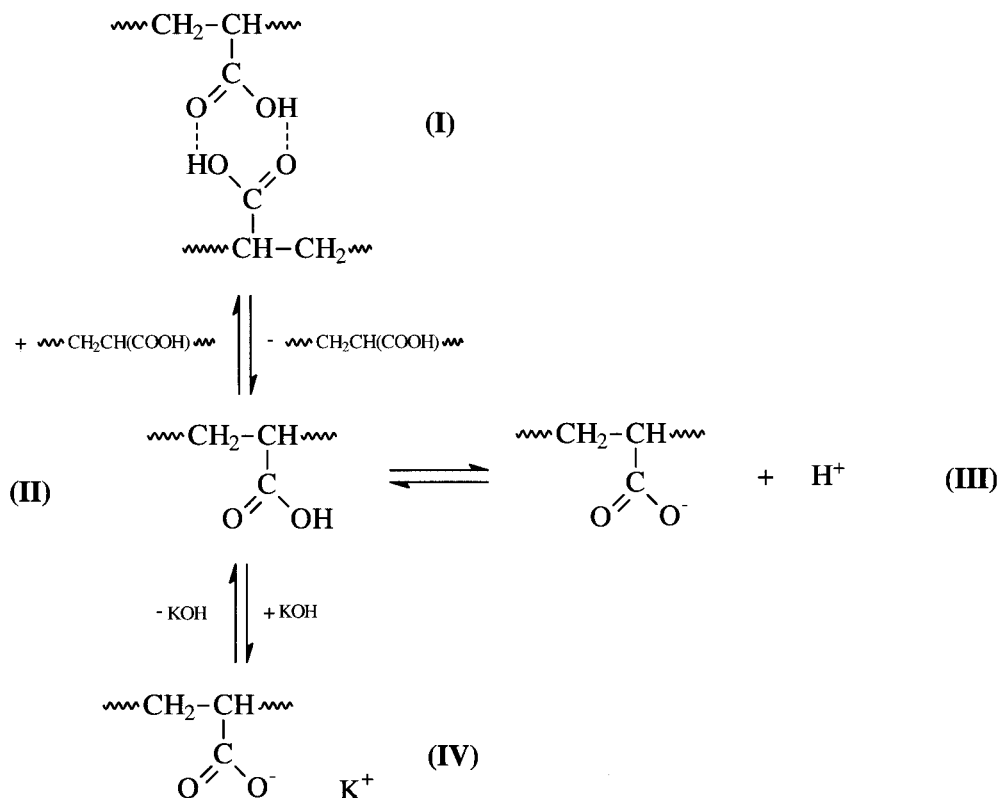
**Figure 7** Scheme representing the relation between dissociation of poly(acrylic acid) and its neutralization. The dotted lines represent hydrogen bonding.

zero, its degree of dissociation tends to 1, one could imagine poly(acrylic acid) at this condition as a fully dissociated polyelectrolyte, so that the solution could be considered as isoionic. By comparison to eq. (5), $k_1$ could be defined as

$$k_1 \equiv \frac{1}{[\eta]^2} \lim_{c_2 \to 0} \frac{d\eta_{\text{red}}}{dc_2} = \frac{1}{[\eta]^2} \lim_{c_2 \to 0} \eta_{\text{red}} \frac{d \ln \eta_{\text{red}}}{dc_2} \qquad (6)$$

Substitution of eq. (3) in eq. (6) yields:

$$k_1 = \frac{1}{[\eta]^2} \lim_{c_2 \to 0} [\eta][a_0 e^{-a_1 \sqrt{c_2}}(1 - a_1 \sqrt{c_2})] = \frac{a_0}{[\eta]} \qquad (7)$$

If this approach were correct, the values of $[\eta]$ and $k_1$ should be independent of $n_{\text{KOH}}/n_{\text{COOH}}$. Figure 6 shows the values of $[\eta]$ and $k_1$ as a function of $n_{\text{KOH}}/n_{\text{COOH}}$ and one can see that, conversely, $k_1$ continuously falls while $[\eta]$ increases with $n_{\text{KOH}}/n_{\text{COOH}}$, so that an alternative approach is necessary.

Regarding ionization versus coil expansion of poly(acrylic acid), the scheme depicted in Figure 7 shows two possible situations which lead a given macromolecule to different conformational situations: structure (I) represents the occurrence of hydrogen bonding between two mere units of a given macromolecule. This interaction would obviously lead to a more con-tracted coil. These hydrogen-bonded units would also be in equilibrium with the non-hydrogen-bonded structure (II) which, of course, would be in equilibrium with its dissociated form (III). Neutralization by KOH would lead, of course, the equilibrium to (IV), increasing the dissociation of the polyacid. As pointed out, if one were dealing with low molecular weight compounds, as concentration tended to zero, the dissociation degree would tend to one; in other words, regardless of the $n_{\text{KOH}}/n_{\text{COOH}}$ ratio, the values of $[\eta]$ should be the same, in opposition to the behavior at higher concentrations, where there is the occurrence of a maximum $\eta_{\text{red}}$. The fact that it was not observed in Figure 6 can be related to the observation that, regarding the carboxyl groups, as concentration decreases, the solutions tend to be less and less regular, because the concentration of these groups within the coils is much higher than the average solution concentration. As a result, one should expect a residual amount of nondissociated carbonyls, even when polymer concentration tends to zero. The increase in the $n_{\text{KOH}}/n_{\text{COOH}}$ ratio would lead, then, to an increase in negative charges along the polymer chain, continuously increasing its volume. Finally, the decrease in $k_1$, suggesting a decrease in interpolymer interactions, could also be linked to the increase in neutralized carbonyl within the polymer chain. This decrease could be re-

lated to a corresponding weakening of the interchain attractive interactions (lower occurrence of hydrogen bonds) or to the formation of a stronger double layer (as established by Manning's theory of counterion condensation[25]), which does not favor energy dissipation through interparticle collisions.

## CONCLUSION

Poly(acrylic acid) viscometry, when carried out at conditions defined as isoionic ones, can be used to study hydrodynamic interactions of these macromolecules. These electrostatic interactions can be divided into intra- and intermolecular ones and it can be confirmed by the occurrence of a maximum in the $\eta_{red} \times$ molar polymer concentration curve. Their behavior can also be related to the degree of dissociation of the polyacid, which can be indirectly monitored by solution conductivity measurements. At very low concentrations, the variation of intrinsic viscosity as well as the Huggins' constant indicates that, even when concentration tends to zero, the polyacid does not tend to be fully dissociated.

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