

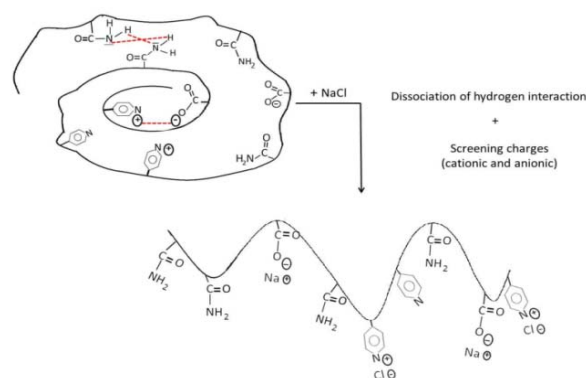
## SYNTHESIS CONDITION EFFECTS ON THE ANTI-POLYELECTROLYTE BEHAVIOUR OF POLY(ACRYLAMIDE-CO-(4-VINYLPYRIDINE)) (AM/4VP) COPOLYMERS IN AQUEOUS MEDIA

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We have synthesized new copolymers **AM/4VP** of acrylamide (AM) and 4-vinylpyridine (4VP) in aqueous solution by radical adiabatic copolymerization. The prepared copolymers were characterised by nuclear magnetic resonance ( $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR), and UV -visible spectrophotometry. The molecular weights were obtained by size exclusion chromatography (SEC), and by viscosity. The reduced viscosity variation of the copolymers aqueous solutions with its concentration showed an anti-polyelectrolyte behaviour in the presence of NaCl salt. This behaviour was explained by an increase of the reduced viscosity ( $\eta_{\text{red}}$ ) in dilute system. Moreover, this phenomenon depended on synthesis conditions, such as the percentage of water and 4-vinylpyridine co-monomer in the mixture at constant values of pH and temperature.



### INTRODUCTION

The viscosity behaviour of neutral or charged polymer solutions has been studied by several authors. Poly(4-vinylpyridine) (P4VP) and poly(acrylamide) (PAM) each one was studied for several decades. In addition, a large number of studies<sup>1-3</sup> have investigated the viscosity of P4VP in various solvents and under various temperatures. The results showed a discontinuity in the intrinsic viscosity variation as a function of the P4VP concentration. In one of our previous work,<sup>4</sup> we have studied the effect of the viscosity parameters as a function of the viscosity macromolecular weight ( $M_v$ ) of P4VP homo-polymers. Thus, we cover all the macromolecular weight range, from 7500 to  $2 \times 10^6$  g/mol, where other values for

viscosity parameters were mentioned. While, for the poly(acrylamide) viscosity studies, we can cite several works and studies.<sup>5-9</sup> Indeed, the viscosity study of the poly(acrylamide-co-(4-vinylpyridine))AM/4VP copolymer was reported in three studies<sup>10-12</sup> without details. Baojiao *et al.*<sup>10</sup> have synthesized poly(acrylamide-co-(4-vinylpyridine)) in organic solvents using potassium persulfate ( $\text{K}_2\text{S}_2\text{O}_8$ ) as initiator. The obtained copolymers have low intrinsic viscosities  $[\eta]$  and therefore low macromolecular weight ( $M_w$ ). However, Gui *et al.*<sup>11</sup> synthesized and characterized a zwitterionic copolymer of acrylamide and 4-vinylpyridine-propyl-sulfo-betaine (AMVPPS) in NaCl solution at 30 °C using potassium persulfate ( $\text{K}_2\text{S}_2\text{O}_8$ ) and sodium bisulphite ( $\text{NaHSO}_3$ ) as initiator. They were found that AMVPPS copolymer was a good

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flocculent for both anionic kaolin and cationic hematite suspensions and the flocculation performance of this copolymer was much better than that of pure poly(acrylamide). For this copolymer (AMVPPS), an Anti-polyelectrolyte behaviour was observed and was found to be enhanced with increasing 4-VPPS ratio. The obtained copolymers have also low intrinsic viscosities  $[\eta]$  and therefore low macromolecular weight ( $M_w$ ). In a previous work,<sup>12</sup> we have studied the viscosity behaviour of a new copolymer based on acrylamide (AM) and 4-vinylpyridine (4VP) co-monomers as shown in (Figure 1), in aqueous solution at 25 °C in the absence and in the presence of NaCl salt. We have observed an anti-polyelectrolyte behaviour in the presence of NaCl salt in aqueous solution. On the other hand, the anti-polyelectrolyte behaviour appears remarkably in dilute regime, by addition of NaCl salt to the aqueous copolymer solutions. This phenomenon was influenced by the pH of the aqueous medium.

The present work is a continuity of the previous one.<sup>12</sup> We focus to study the effect of the water and 4-vinylpyridine co-monomer percentage on the anti-polyelectrolyte behaviour in this set of AM/4VP copolymers. Optimization of this phenomenon was possible by investigating the influence of different parameters.

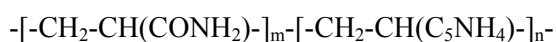


Fig. 1 – Chemical structure of the copolymer AM-4VP.

## RESULTS AND DISCUSSION

### Water percentage effect

In this part of our work, the mass percentage of co-monomers (AM and 4VP) are fixed in the mixture at a rate of 14/1 (AM14/4VP1), while the mass percentage of water is variable. The obtained results are depicted in Figure 2. Figures 2a, 2b and 2c represent the change in reduced viscosity of the copolymers AM14/4VP1 according to their concentrations at  $T = 25$  °C in the absence and the presence of NaCl salt for different percentages of water (co-monomers/water ratio: (a): (70/30), (b): (50/50) and (c): (30/70)) at pH= 6.

**In the absence of NaCl salt**, the copolymers AM14/4VP1 (70/30), AM14/4VP1 (50/50) and AM14/4VP1 (30/70) show a weakly charged polyelectrolyte behaviour. However in the case of AM14/4VP1 (50/50), this phenomenon was more pronounced. This result can be explained by the

hydrolysis effect of acrylamide functions meaning the presence of carboxylate functions in the copolymer chains<sup>12</sup> and leading to the associative effect of the hydrophobic segments in the copolymer.

For the copolymer AM14/4VP1 (70/30) (Figure 2a), at the beginning, we observed an increase in the reduced viscosity which is followed by a low decrease. Beyond a certain concentration, the shape of the curve is that of neutral polymer. However, for the copolymer AM14/4VP1 (50/50) (Figure 2b), the polyelectrolyte effect was more pronounced. In dilute regime at low concentrations, the copolymer showed an increase in reduced viscosity to reach a maximum at  $C_p = 10^{-4}$  g/mL which was followed by a decrease in the reduced viscosity values. This phenomenon was observed in the case of polyelectrolyte with high macromolecular weight. However, it was not detectable for polyelectrolyte with low macromolecular weight.<sup>13,14</sup> In this case, the hydrophobic interactions were favored when the concentration increases which causes a relaxation of chains and the reduced viscosity decreased. Beyond  $C_p = 1.2 \times 10^{-3}$  g/mL, the curve of variation reveals a progressive increase in the reduced viscosity as a function of the copolymer concentration. The copolymer chains are entangled like in the neutral polymer chains. They formed a temporary's cross-linking and the viscosity increased.

For the copolymer AM14/4VP1 (30/70) as can be seen in Figure 2c, a slight decrease was observed in the reduced viscosity, at the beginning. Beyond a certain copolymer concentration, the curve has the shape like that the neutral copolymer. If we compare the reduced viscosity values of these three copolymers for the same concentration, we found that the viscosity of the copolymer AM14/4VP1 (50/50), majored throughout the concentration range.

**In the presence of NaCl salt**, the curve has two variation ranges, depending on the copolymer concentrations in all studied cases. But, the larger of each area was specific for each copolymer.

First, for the copolymers AM14/4VP1 (70/30) (Figure 2a) and AM14/4VP1 (30/70) (Figure 2c), the reduced viscosity of the copolymer solutions was modified by the presence of NaCl salt. Indeed, for low concentrations of copolymers  $C_p < 2,5 \times 10^{-4}$  g/mL for AM14/4VP1 (70/30) and  $C_p < 7,5 \times 10^{-4}$  g/mL for AM14/4VP1 (30/70), we note an increase in the reduced viscosity with increasing NaCl concentration in the mixture. We are effectively in the presence of an anti-polyelectrolyte phenomenon.<sup>15-17</sup> This phenomenon has been noticed in the case of zwitterionic copolymers and in the case of polyacrylamide (PAM) solutions in

the presence of salt. Authors attribute this phenomenon, in the case of the PAM, to the dissociation of hydrogen bonds following the addition of salt.<sup>13</sup> While in the case of zwitterionic copolymers, this phenomenon was attributed to the charges screening and to the attractive electrostatic interactions between cationic and anionic group's which decreased, causing an extension of the copolymer chains and the viscosity increased.<sup>11,15-17</sup> In our case, we can explain this phenomenon by two suppositions:

Firstly, the formation of micro-domains in the mixture and the addition of NaCl salt caused an infiltration of water inside these micro-domains. Thus, their volumes increased leading to an increase in reduced viscosity (dilute system).

Secondary, our copolymer has a zwitterionic properties following the simultaneous presence of

a low percentages of carboxylate ( $\text{COO}^-$ ) and pyridinium ( $4\text{VP-N}^+$ ) functions. In fact, this behaviour depends on the pH isoelectric value of the copolymer which is between 6 and 6.4 as predetermined for other similar copolymers.<sup>18,19</sup> The salt addition leads to the screening of the oppositely charges in the copolymer. This phenomenon caused an extension of the chains, mostly when the copolymer chains have enough space (dilute regime). However, for  $C_p > 2.5 \times 10^{-4}$  g/mL of AM14/4VP1 (70/30) and  $C_p > 7.5 \times 10^{-4}$  g/mL of AM14/4VP1 (30/70), the addition of NaCl salt caused a decrease in the reduced viscosity. The screening phenomenon was predominant in this case. It can be explained by the screening of residual charge  $\text{N}^+$  of the pyridine leading to the occurrence of attractive interactions between the aromatic cycles of 4-vinylpyridine.

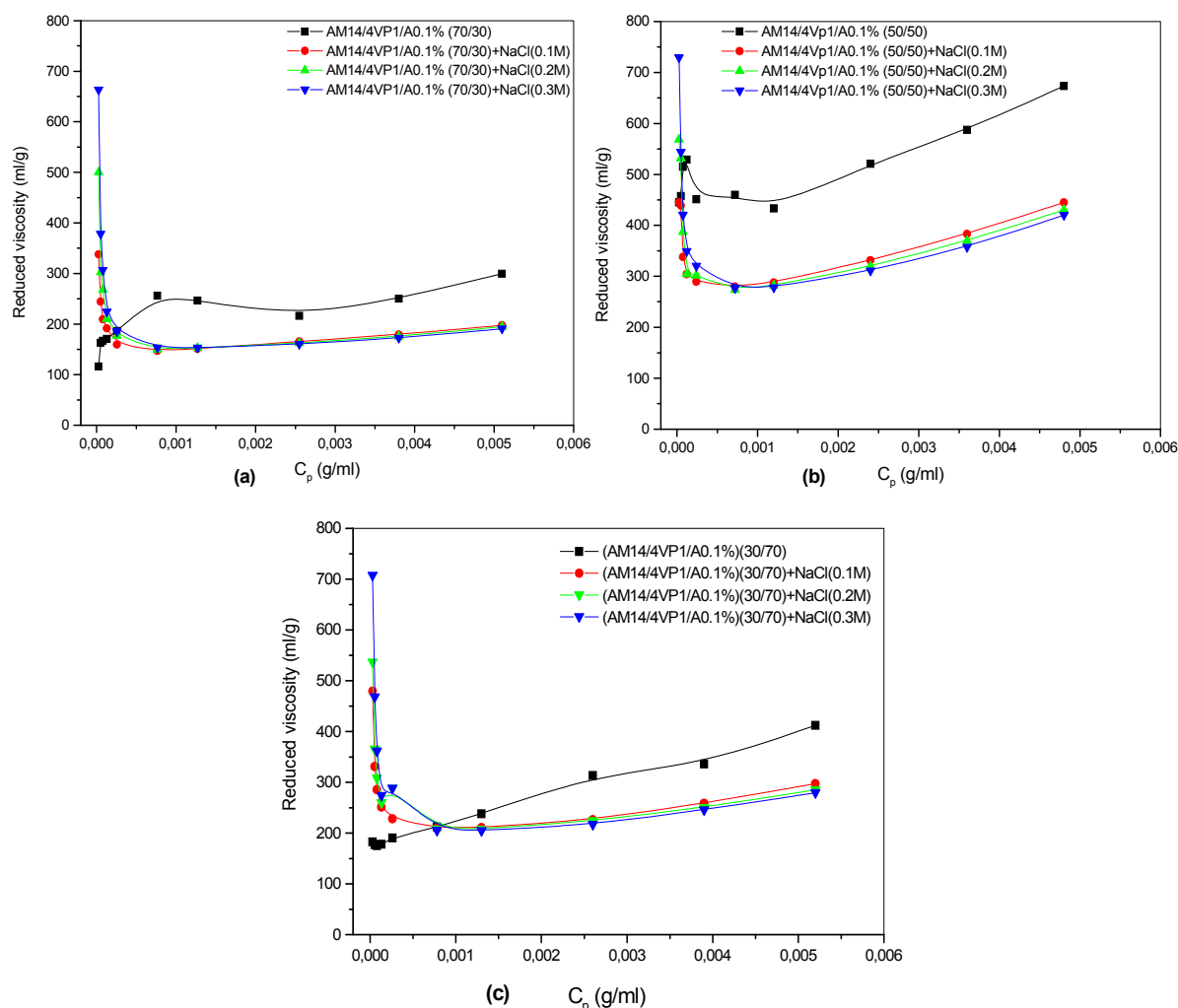
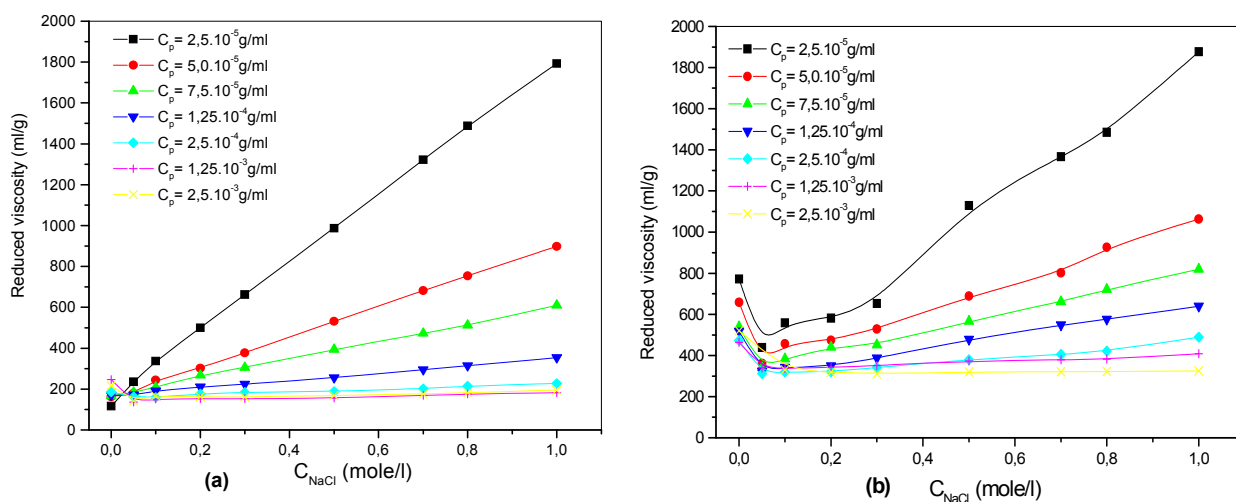


Fig. 2 – Reduced viscosity variation of the copolymer **AM14/4VP1** as a function of its concentration in the absence and in the presence of NaCl salt for different percentages of water at 25 °C and pH = 6: (70/30) (a); (50/50) (b); (30/70) (c).

Table 1

Viscosity results of copolymers obtained in bi-distilled water at 25 °C and pH=6

Copolymer	AM14/4VP1 (70/30)	AM14/4VP1 (50/50)	AM14/4VP1 (30/70)
Percentage of initiator (A %)	0.1	0.1	0.1
$[\eta]$ in the absence of NaCl (mL/g)	180	360	155
$M_v \times 10^{-5}$ in the absence of NaCl (g/mol)	5	12	2.2
$[\eta]$ in the presence of 0.1M NaCl(mL/g)	150	250	200
$M_v \times 10^{-5}$ in the presence of 0.1M NaCl (g/mol)	4	7.7	5.8
$M_w \times 10^{-5}$ by CES (g/mol)	4.9	15	9.5
The presence of polyelectrolyte behavior in the absence of NaCl	Very weak	Yes	Very weak
The presence of anti-polyelectrolyte behavior in the presence of NaCl	Yes	No (or very weak)	Yes

Fig. 3 – Reduced viscosity variation of the copolymers according to salt concentration ( $C_{NaCl}$ ) for various copolymer concentrations in bi-distilled water at 25 °C and pH = 6: AM14/4VP1 (70/30) (a); AM14/4VP1 (50/50) (b).

For the copolymer AM14/4VP1 (50/50) depicted in (Figure 2b), the anti-polyelectrolyte behavior was almost missing because the copolymer has a polyelectrolyte effect in the absence of NaCl salt. In fact, a pronounced decrease in the viscosity was observed when the copolymer concentration increased. Addition of NaCl increased the ionic strength of the solution, thus causing contraction of copolymer chains. This behavior has been reported by several authors.<sup>7,13</sup> From the (Figure 2a, 2b and 2c), we can deduce some viscosity results. (Table 1) gives the obtained results of intrinsic viscosity  $[\eta]$  in the absence and in the presence of NaCl salt, the viscosity molecular weight of the copolymer ( $M_v$ ) values and the weight-average molar mass ( $M_w$ ) which was obtained using size exclusion chromatography (SEC) for the studied copolymers.

When we compare  $M_v$  value with the weight-average molar mass ( $M_w$ ), we note that the macromolecular weight  $M_w$  and  $M_v$  in the presence of salt are in very good agreement.<sup>20</sup> It should be also noted that the percentage of water affected the anti-polyelectrolyte behaviour.

To explain this anti-polyelectrolyte phenomenon, a detailed viscosity study for two copolymers (AM14/4VP1(70/30) and AM14/4VP1(50/50)) in the presence of different concentrations of (NaCl) salt was carried out. Figure 3a and 3b showed the variation of the reduced viscosity (at 25 °C in bi-distilled water) of AM14/4VP1 (70/30) and AM14/4VP1 (50/50) copolymers according to the NaCl salt concentration for various copolymer concentrations at pH of the medium equal to 6.

For the copolymer AM14/4VP1 (70/30) depicted in Figure 3a, the anti-polyelectrolyte

behaviour was more pronounced than the AM14/4VP1 (50/50) copolymer (Figure 3b). For low copolymer (AM14/4VP1 (70/30)) concentration, we observed a strong increase in the reduced viscosity. For example,  $C_p = 2.5 \times 10^{-5}$  g/mL, the reduced viscosity values pass from 116 to 1800 mL/g when the NaCl salt concentration pass from 0 to 1 mol/L. In addition, for the same copolymer (AM14/4VP1 (50/50)) concentration, the reduced viscosity increased strongly (about 1000 mL/g) as the NaCl concentration value rose from 0 to 1 mol/L. However, for the copolymer AM14/4VP1 (50/50), the curves have the same pace. At the beginning, a fall in reduced viscosity values to reach a minimum for a concentration of NaCl salt equal to 0.05 M for various copolymer concentrations. It can be explained by the phenomenon of screening charges of the carboxylate functions present in the copolymer. This finding confirms the polyelectrolyte behavior of the AM14/4VP1 (50/50) copolymer. Indeed, this minimum is followed by an increase of reduced viscosity according to NaCl salt concentration. On the other hand, this reduced viscosity strongly increases (in both cases) when the copolymer concentration decreases. These results correlate favourably with the previous viscosimetric results.

#### 4-vinylpyridine percentage effect

However, in this second part of this work, the mass percentage of water is fixed in the mixture and the mass percentage of co-monomers (AM and 4VP) are variable. The obtained results are shown in (Figures 4 and 5).

Figures 4a and 4b represent the variation of reduced viscosity of the copolymer AM<sub>x</sub>/4VP<sub>y</sub> (50/50) according to its concentration in the

absence and in the presence of NaCl salt for different percentage of co-monomers at 25 °C and pH = 6. It was found that the curves have the same pace. The copolymers (AM14/4VP1/A0.1% (50/50) and AM14/4VP0.5/A0.1% (50/50)) exhibited a polyelectrolyte behavior in the presence and in the absence of NaCl salt. The added of salt caused a decrease of reduced viscosity, the anti- polyelectrolyte behaviour was almost absent. However, Figures 5a and 5b represent the variation of reduced viscosity of the copolymer AM<sub>x</sub>/4VP<sub>y</sub> (70/30) according to its concentration in the absence and in the presence of NaCl salt for different percentage of co-monomers at 25 °C and pH = 6.

It can clearly be observed on the representative curves that the copolymers (AM14/4VP1/A0.1% (70/30) and AM14/4VP5/A0.1% (70/30)) showed weakly charged polyelectrolyte behaviour in the absence of NaCl salt. While, in the presence of NaCl salt the two copolymers showed an anti-polyelectrolyte behaviour. The added of salt for weak concentration of two copolymers caused an increase of reduced viscosity. The result deduced from Figures 4 and 5 confirms the presciently results. It should be also noted that the percentage of 4-vinylpyridine (or co-monomers generally) do not affected the anti-polyelectrolyte behaviour. Table 2 gives the obtained result of intrinsic viscosity  $[\eta]$  in the absence and the presence of NaCl salt, the viscosimetric molecular weight of the copolymers ( $M_v$ ) values and the weight-average molar mass ( $M_w$ ) which was obtained using size exclusion chromatography (SEC) for the studied copolymers. Note also, that the percentage of 4-vinylpyridine in the copolymer affected the values of molecular weight  $M_w$  and  $M_v$ . This result is in accordance with the previous results.<sup>20</sup>

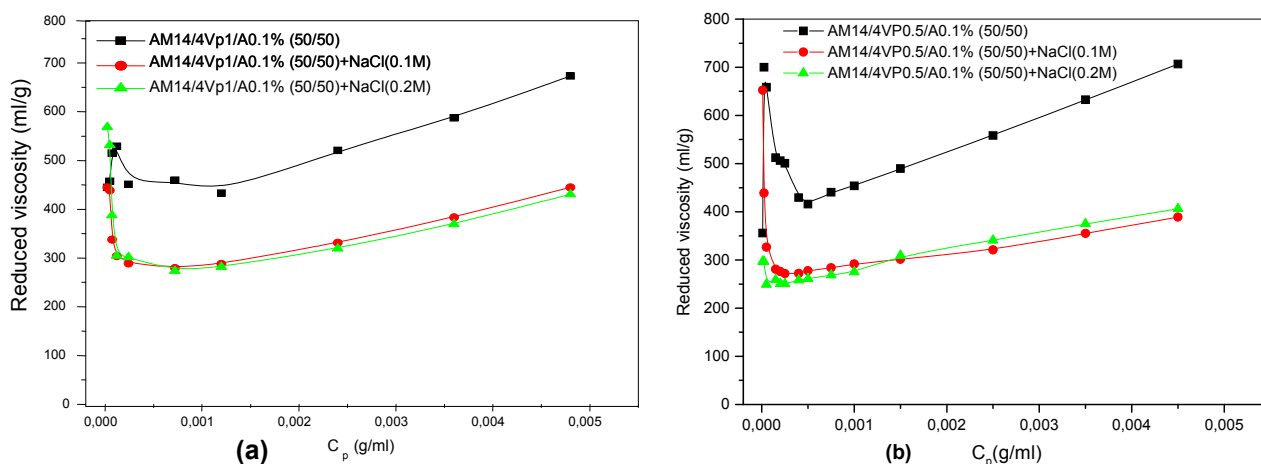


Fig. 4 – Reduced viscosity variation of the copolymer AM<sub>x</sub>/4VP<sub>y</sub> (50/50) as a function of its concentration in the absence and in the presence of NaCl salt for different percentages of co-monomers at 25 °C and pH = 6: AM14/4VP1 (a); AM14/4VP0,5 (b).

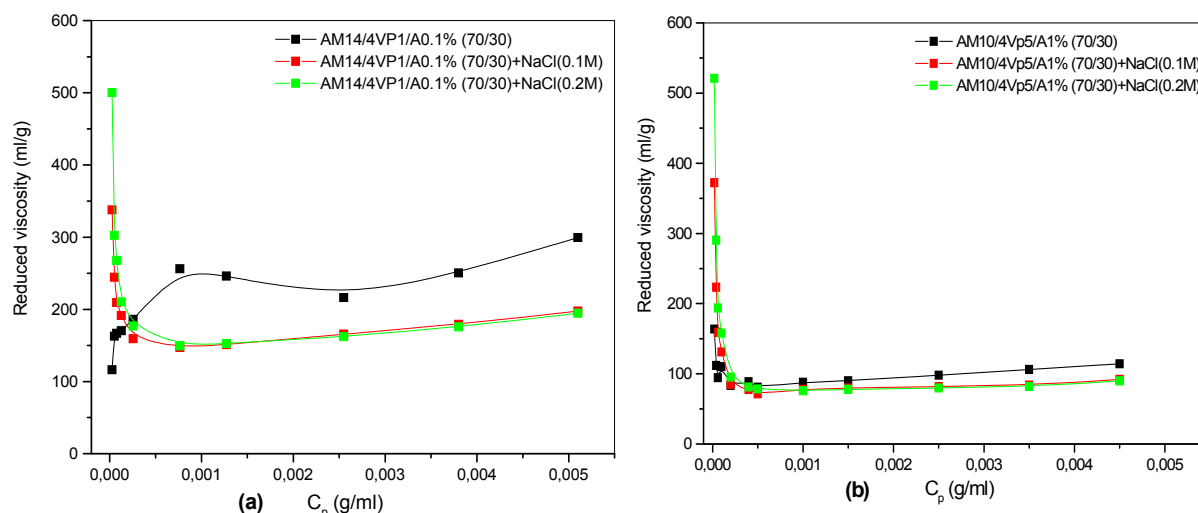


Fig. 5 – Reduced viscosity variation of the copolymer AM<sub>x</sub>/4VPy (70/30) as function of its concentration in the absence and in the presence of NaCl salt for different percentages of co-monomers at 25 °C and pH = 6: AM14/4VP1 (a); AM10/4VP5 (b).

Table 2

Viscosity results of copolymers obtained in bi-distilled water at 25 °C and pH = 6

Copolymer	AM14/4VP1 (50/50)	AM14/4VP0.5 (50/50)	AM14/4VP1 (70/30)	AM10/4VP5 (70/30)
Percentage of initiator (A%)	0.1	0.1	0.1	1
$[\eta]$ in the absence of NaCl (mL/g)	360	370	180	88
$M_v \times 10^{-5}$ in the absence of NaCl (g/mol)	12	12.3	5	2.1
$[\eta]$ in the presence of 0.1 M NaCl (mL/g)	250	270	150	74
$M_v \times 10^{-5}$ in the presence of 0.1 M NaCl (g/mol)	7.7	8.4	4	1.7
$M_w \times 10^{-5}$ by CES (g/mol)	15	16	4.9	2,6
The presence of polyelectrolyte behavior in the absence of NaCl	Yes	Yes	Very weakly	Very weakly
The presence of anti-polyelectrolyte behavior in the presence of NaCl	No (or very weakly)	No (or very weakly)	Yes	Yes

## MATERIALS AND METHODS

### Materials

Acrylamide (AM) was provided from Merck. 4-vinylpyridine (4VP) (Aldrich, 98%) was treated according to the procedure described in our earlier work.<sup>20</sup> Ammonium persulfate (APS) (Aldrich) was used as initiator without further purification, however, the bi-distilled water was used as solvent.

### Methods

#### *Copolymerisation of Acrylamide (AM) and 4-vinylpyridine (4VP)*

The radical adiabatic copolymerization was realised in a reactor (Dewar). The monomers,

acrylamide (AM) and 4-vinylpyridine (4VP) were dissolved in bi-distilled water. The aqueous ammonium persulfate (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> was added as initiator. The synthesis and the purification of our copolymer were carried out according to the method described in our earlier work.<sup>20</sup> The copolymer is noted [AM<sub>x</sub>/4VP<sub>y</sub>/A%(X/Y)] knowing that the constituents of this copolymer are: AM<sub>x</sub>: x g of AM, 4VP<sub>y</sub>: y g of 4-vinylpyridine, A%: mass percentage of initiator compared to that of co-monomers (AM<sub>x</sub>+ 4VP<sub>y</sub>), X: mass percentage of co-monomers (AM<sub>x</sub>+ 4VP<sub>y</sub>) in the mixture, Y: mass percentage of water in the mixture.

#### *Characterization of the copolymer*

<sup>1</sup>H NMR: <sup>1</sup>H NMR spectra were carried out using Bruker Advance 400 spectrometer in



D<sub>2</sub>O/DCl as solvents. <sup>1</sup>H chemical shifts are as follows:

1.23 - 1.59 ppm with a maximum at 1.46 ppm (–CH<sub>2</sub>–) of the linear chains of the copolymer.<sup>20,21</sup>

1.88 - 2.19 ppm with a maximum at 2.04 ppm (–CH–) of the linear chains of the copolymer.<sup>20,21</sup>

4.41 - 4.72 ppm (solvent protons)

The use of the D<sub>2</sub>O/DCl solvent led to a nitrogen quaternization in the aromatic cycles and consequently their protons were deblinded.<sup>20,22</sup>

6.8 ppm (H atom at ortho position of N atom of the 4VP ring).

7.5 - 7.8 ppm (H atom at the meta position of N atom and the ortho position of N<sup>+</sup> of the 4VP rings).

8.53 ppm (H atom at the meta position of N<sup>+</sup> atom of the 4VP ring).

**<sup>13</sup>C NMR:** <sup>13</sup>C NMR spectra characterisations of the copolymer were recorded using Bruker Avance 400 spectrometer in D<sub>2</sub>O as solvent. <sup>13</sup>C chemical shifts are as follows:

179.63 ppm the carbon of the acrylamide carbonyl function.

41.42 - 42.08 ppm and 33.73 - 35.83 the carbons of acrylamide linear chains.

148.73 ppm and 124.07 ppm the carbons of aromatic cycle of 4-vinylpyridine.<sup>20,23,24</sup>

**UV-visible spectra:** The UV-visible absorption spectra were carried out using OPTIZEN 2120 UV-VIS spectrophotometer located in Laboratory of Organic Electrolytes and Polyélectrolytes' Application (LAEPO), University of Tlemcen, Algeria. The solvent was bi-distilled water. The spectra of the copolymer showed an intense absorption at 256nm corresponding to the n→π\* band of 4VP monomer. This result is fully compliant with the results of Bernard et al.<sup>25</sup> and confirm the presence of the 4-vinylpyridine in the copolymer. However, the acrylamide monomer has not any absorption in the 256 nm area.

#### Macromolecular weight characterization:

The macromolecular weight was estimated by two methods; the first one is the viscosity technique using bi-distilled water as solvent. An Ubbelohde capillary viscometer (SHOTT AVS 360), with a thermo-stated bath at 25 ± 0.1°C was used in our laboratory. The reduced viscosity  $\eta_{red}$ , the intrinsic viscosity  $[\eta]$  and the viscosimetric molecular weight of the copolymer ( $M_v$ ) were determined according to the method described in our previous paper.<sup>20</sup> The second is the size exclusion chromatography (SEC) by using a Waters Alliance

2690 equipped with Waters Ultra-hydro-gel 250, 500 and 2000 and refractive-index (RI) detector, in the (IPREM), University of Pau, France. The number and the weight average molecular weights ( $M_n$  and  $M_w$ ) and molecular weight distributions ( $I_p = M_w/M_n$ ) were determined. The set-up we used was detailed in our previous work.<sup>20</sup>

## CONCLUSIONS

In this study, the AM/4VP copolymers were prepared by radical adiabatic copolymerization in aqueous solution. The resulting copolymers were characterized by nuclear magnetic resonance (<sup>1</sup>H NMR and <sup>13</sup>C NMR), and UV-visible spectrophotometry. The main objective of this work was to study the effect of the percentage of water and 4-vinylpyridine co-monomer in the anti-polyelectrolyte behaviour of this copolymers series. This study was realized in aqueous media in the absence and in the presence of NaCl salt at 25°C and at pH = 6, allows us to deduce the following conclusions: (i) The anti-polyelectrolyte behaviour was manifested by an increase in the reduced viscosity by addition NaCl salt to the copolymer. (ii) The presences of different constituents (acrylamide, 4-vinylpyridine, acid acrylic and acrylate) in this copolymer were mainly responsible for the anti-polyelectrolyte behaviour. (iii) The percentage of 4-vinylpyridine (or co-monomers generally) do not affected the anti-polyelectrolyte behaviour while the percentage of water affects the anti-polyelectrolyte behaviour and the macromolecular weight  $M_w$  and  $M_v$  for the same quantity of initiator.

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