

## Conductimetric and Tensiometric studies of acrylamide-co-4vinylpyridine (AM-4VP-9) copolymer in aqueous media

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### Abstract

A copolymer of acrylamide (AM) and 4-vinylpyridine (4VP) (**POLY(AM-CO-4VP)**) was synthesized by radical adiabatic copolymerization in aqueous solution. The synthesized copolymer was identified by <sup>1</sup>H NMR, <sup>13</sup>C NMR, UV-visible spectra and conductimetry. The molecular weights are obtained by GPC and viscosity. The conductimetry measurement showed that the copolymerisation methods caused a hydrolysed acrylamide function. On the other hand the variation of the surface tension of aqueous copolymer solutions with copolymer concentration revealed a surfactant behavior of the copolymer. The obtained result was compared to that of surfactant model N-dodecyl-pyridinium chloride (**DPC**). This surfactant behavior of the copolymer according to the neutralization degree  $\alpha$  was also investigated by surface tension measurements.

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## 1. Introduction

Polyelectrolyte solutions have been studied extensively for both theoretical and experimental purposes. Due to electrostatic interactions between the charged groups along the polyelectrolyte chains, its solutions behaves differently than the neutral polymers for activity coefficients, osmotic coefficients, as well as transport properties like, viscosity, diffusion, etc. [1–4]. Among the many water-soluble polymers available, copolymers and homopolymers based on Acrylamide (AM) are widely used in many fields and in the past few years the study of copolymerization of Acrylamide with functional monomers has attracted increasing attention [5–7]. Cationic and multiple-functional polyacrylamide (PAM) is an important reagent in industry for wastewater treatment due to the excellent flocculation function originating from synergistic effects of charge neutralization and bridging adsorption [8–10]. The poly(acrylamide-co-4-vinylpyridine) copolymers have a vast array of applications. They are used in drug and gene delivery systems as flocculants [11], as retention agent of metals [12] and as corrosion inhibition agent [13, 14]. The physicochemical properties of these copolymers depend not only on the structural parameters of the copolymer such as the macromolecular weight, the percentage of 4-vinylpyridine and acrylamide comonomers but also on environmental parameters (pH, salinity, temperature, etc.) [15, 16]. In a previous paper [15], we have described the synthesis and the chemical characterization of this new copolymer AM-4VP-9. We have investigated the effect of iodide ions on the corrosion inhibition of mild steel in 1 M sulfuric acid in the presence of the copolymer (AM-4VP-9) by weight loss measurements and potentiodynamic polarization at 18°C. It's found that the copolymer was an excellent corrosion inhibition of mild steel in H<sub>2</sub>SO<sub>4</sub> 1 M [17]. We have also studied the variation of the reduced viscosity of aqueous copolymer (AM-4VP-9) solutions with copolymer concentration. It's showed an anti-polyelectrolyte behaviour in aqueous solution in presence of NaCl salt. This phenomenon depended on the pH of the aqueous medium. The determination of the viscosimetric macromolecular ( $M_v$ ) is established using Mark Howink equation of polyacrylamide which is compared with macromolecular weight ( $M_w$ ) obtained by GPC [16]. To complete the studied of this copolymer, in the present work we report the conductimetric and surface tension measurements of the AM-4VP-9 copolymer, in aqueous solution at T = 25 °C. The aim of combine of physicochemical measurement in aqueous solution and at the interface is to obtain an overall picture of the copolymer. Thus, the obtained results of the surface tension measurements were compared to those of a model surfactant, N-dodecyl-pyridinium chloride (DPC).

## 2. Experimental section

### 2.1. Products and reagents

Acrylamide (AM) was provided from Merck. 4-vinylpyridine (4VP) (Aldrich, 98%) was dried over calcium hydride overnight and fractionally distilled under reduced pressure (68°C- 69°C at 15mmHg), having discarded the first and last 10% of the monomer. Ammonium persulfate (Aldrich) was used as initiator without further purification. Water used was bidistilled.

### 2.2. Copolymerisation of AM and 4VP

Copolymerization were realised in a reactor (dewar) when acrylamide (AM) and 4-vinylpyridine (4VP) were dissolved in bidistilled water. The mixture was stirred and purged with N<sub>2</sub> for 15 minutes, and then aqueous ammonium persulfate (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> was added as initiator. One starts the reaction by rapid heating of the mixture. Then, the obtain copolymer was dissolved in water and precipitated in acetone or ethanol repeatedly. The product was then dried under vacuum at room temperature to constant weight and stored in a desiccator [15].

## 2.3. Characterisation of the copolymer

### 2.3.1. $^1\text{H}$ NMR

$^1\text{H}$  NMR (400 MHz) spectra were recorded on a Bruker Avance 400 spectrometer. The solvents were  $\text{D}_2\text{O}/\text{DCl}$ .

$^1\text{H}$  chemical shifts ( $\text{CH}_3\text{OD}$ ) are as follows:

- 1.23-1.59 ppm with a maximum at 1.46 ppm ( $-\text{CH}_2-$ ) of the linear chains of the copolymer [11, 15, 18].
- 1.88-2.19 ppm with a maximum at 2.04 ppm ( $-\text{CH}-$ ) of the linear chains of the copolymer [11, 15, 18].
- 4.41-4.72 ppm (solvent protons)
- For the aromatic protons, we distinguish four types of proton. The use of the  $\text{D}_2\text{O}/\text{DCl}$  solvent led to a quaternisation of the cycles and consequently their protons will be deblinded [11, 15, 19, 20].
- 6.8 ppm (H atom at ortho position of N of 4VP).
- 7.5-7.8 ppm (H atom at the meta position of N and the ortho position of  $\text{N}^+$  of 4VP).
- 8.53 ppm (H atom at the meta position of  $\text{N}^+$  of 4VP).

### 2.3.2. $^{13}\text{C}$ NMR

$^{13}\text{C}$  NMR (100 MHz) spectra were recorded on a Bruker Avance 400 spectrometer. The solvent was  $\text{D}_2\text{O}$ .

$^{13}\text{C}$  chemical shifts ( $\text{CH}_3\text{OD}$ ) are as follows:

- The peak at  $\delta = 179,63$  ppm is ascribed to the carbon of carbonyl function of acrylamide.
- The peaks at  $41,42 < \delta < 42,08$  ppm and  $33,73 < \delta < 35,83$  are ascribed to the carbon of linear chains of acrylamide.
- The peaks at  $\delta = 148,73$  ppm and  $\delta = 124,07$  ppm in copolymer spectra are ascribed to the carbon of aromatic cycle of 4-vinylpyridine [15, 21-23].

### 2.3.3. UV-visible spectra

The UV-visible absorption spectra were recorded with a PERKIN ELMER LAMDA 800 spectrophotometer. The solvent was bidistilled water.

The presence of the 4-vinylpyridine in the copolymer is confirmed by UV-visible spectrum. The monomer of the 4VP shows an intense absorption at 256nm which is connected to  $\pi-\pi^*$  band which is in agreement with the results of Bernard et al [24]. However the acrylamide monomer does not any absorption in this area [15].

### 2.3.4. Macromolecular weight characterisation

The molecular weight was estimated by the viscosity technique using bidistilled water as solvent and GPC.

#### 2.3.4.1. Viscosity determination

The viscosity of the copolymer was measured in bidistilled water with a standard Ubbelohde capillary viscometer, with a thermostated bath at  $25 \pm 0.1$  °C [16]. The reduced viscosity  $\eta_{\text{red}}$  (ml/g) of the copolymer solution was measured at the desired concentration (g/ml) in NaCl 0.1M aqueous solution. The intrinsic viscosity  $[\eta]$  was obtained by extrapolation to zero concentration and the viscosimetric molecular weight of the copolymer ( $M_v$ ) was determined by using Mark-Houwink equation of polyacrylamide [15, 16]. The obtained results are gives in Table. 1.

**Table 1:** Viscosimetric results of copolymers obtained in bidistilled water at 25°C [15].

| Copolymer | Conversion rate % | $M_v$ in absence of NaCl (g/mole) | $M_v$ in presence of NaCl (g/mole) | Precipitation (sol / non sol) |
|-----------|-------------------|-----------------------------------|------------------------------------|-------------------------------|
| AM-4VP-9  | 90                | $1,2 \cdot 10^6$                  | $7,7 \cdot 10^5$                   | W/EtOH or Acetone             |

#### 2.3.4.2. Water size exclusion chromatography (GPC)

Number and weight average molecular weights,  $M_n$  and  $M_w$ , respectively and molecular weight distributions  $I_p = M_w/M_n$  were determined by size exclusion chromatography (SEC) using a Waters Alliance 2690 equipped with Waters Ultrahydrogel 250, 500 et 2000 and refractive-index (RI) detector. The equipment was calibrated with polyethyleneoxide (PEO) standards, and  $\text{NaNO}_3$  at  $0.1 \text{ mol L}^{-1}$  was used as the eluent with  $0.5 \text{ mL min}^{-1}$  flow.

The weight-average molar mass was obtained by use of a light-scattering spectrophotometer from Brice-Phenix. Table 2 gives the obtained results.

**Table 2.** GPC results

| Copolymer | Conversion<br>rate % | $M_w$ (GPC) (g/mole) | $M_n$ (GPC) (g/mole) | $I_p$ | Precipitation<br>(solvent / no solvent) |
|-----------|----------------------|----------------------|----------------------|-------|---|
| AM-4VP-9  | 90                   | $1,5 \cdot 10^6$     | $8,7 \cdot 10^5$     | 1,72  | W/EtOH or Acetone                       |

#### 2.3.5. Conductivity measurements

The conductivity was measured by use of a CDM 210 conductimeter (Radiometer, Meter Lab.). The solutions studied were contained in a cell glass with double thermostated wall maintained at  $25 \pm 0.1 \text{ }^\circ\text{C}$  by use of a circulating thermostat.

#### 2.3.6. Preparation of solutions for conductivity measurements

The studied solution was prepared by dissolution of a small amount ( $m = 0.025 \text{ g}$ ) of the copolymer in 50 ml of NaOH solution  $10^{-2} \text{ M}$  which will be calibrated by HCl acid  $10^{-2} \text{ M}$  (a strong acid).

#### 2.3.7. Surface tension measurements

The equilibrium surface tension of the aqueous solutions was measured according to the Wilhelmy technique (Gibertini TSD digital Tensiometer). The glass plate was cleaned before each measurement by immersion in ethanol and in bi-distilled water followed by heating. The surface tension,  $\gamma$  (mN/m), was measured under controlled temperature ( $T = 25 \text{ }^\circ\text{C}$ ) as a function of time.

#### 2.3.8. Dilutions

The solutions of various concentrations were prepared by dilutions from copolymer mother solution. They are agitated during at least 2 h to homogenize them before using them in tension surface measurements.

### 3. Results and discussion

#### 3.1. Conductimetric determination of hydrolysis rate

The ionic conductivity is explained by the movement of ions in solution under the influence of an electric field. The main purpose of this study is to verify the neutrality of the obtained copolymers by this method of copolymerization and to determine the weight percentage of the components of the copolymers. The conductimetric titration of the copolymer solutions is done by acids solutions. Using the plot of the conductivity as a function of the volume of the titrant, we can determine the content of the copolymer of acrylate groups [25]. This method is used to measure the carboxylate functions of the copolymer with acid solution ( $\text{HCl } 10^{-2} \text{ M}$ ) [26]. It was also used to determine the degree of hydrolysis in the case of the polyacrylamide obtained by the same adiabatic polymerization technique used in this

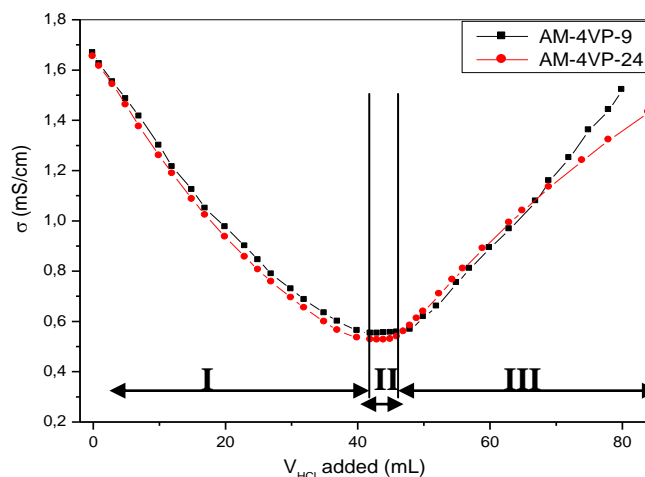
work [27]. The question which arises is: this method of copolymerisation caused a hydrolysed acrylamide function or another effect. To answer this question, we will take two copolymers containing different percentage of acrylamide (AM) and 4 vinylpyridine (4VP), AM-4VP-9 and AM-4VP-24. Table. 3 gives the different percentage of acrylamide (AM) and 4 vinylpyridine (4VP) in copolymers Obtained by NMR  $^1\text{H}$  and UV-Visible.

**Table 3:**  $^1\text{H}$  NMR and UV-visible results

| Copolymers | Conversion<br>rate % | w/w% of AM/4VP<br>( $^1\text{H}$ NMR) final | w/w% of AM/4VP with<br>(UV-Visible) final |
|------------|----------------------|---|---|
| AM-4VP-9   | 90                   | 91,5 / 8,5                                  | 91,7 / 8,3                                |
| AM-4VP-24  | 90                   | 75,6/24,4                                   | 75,9 / 24,1                               |

A conductivity study was performed with the copolymers. The effect of HCl added on the conductivity behaviour of AM-4VP-9 was compared with that of AM-4VP-24. (Fig. 1). Fig. 1 represents the variation of the conductivity of the AM-4VP-9 and AM-4VP-24 copolymers dissolved in  $\text{NaOH } 10^{-2} \text{ M}$  solutions as a function of added acid volume.

In both cases studied, we note the presence of three areas of variation of conductivity as a function of added acid volume. The conductivity of the copolymers solutions is modified by the addition of HCl solution. Indeed, the curves fall at the beginning to reach a minimum at 41.5mL of HCl solution (area I). The very rapid change is because of the strong interaction between the  $\text{H}^+$  ions and the  $\text{OH}^-$  ions in excess in the medium. In this case all  $\text{OH}^-$  ions are protonated.



**Figure 1:** Conductivity dosages of copolymers dissolved in  $\text{NaOH } 10^{-2} \text{ M}$  with  $\text{HCl } 10^{-2} \text{ M}$  at  $25^\circ\text{C}$ .

There is subsequently a small plateau (area II), which can be connected to the protonation of carboxylate function ( $\text{RCOO}^-$ ) or the quaternization of 4VP by  $\text{H}^+$  ions of HCl acid. Indeed, the larger of this plateau is different for the tow copolymers. Finally, we observe a sharp increase in conductivity which corresponds to the excess of  $\text{H}^+$  ions introduced by HCl solution in the medium (area III). The second question which arises is: This plateau (area II) is connected to the protonation of carboxylate function ( $\text{RCOO}^-$ ) or the quaternization of 4VP by  $\text{H}^+$  ions of HCl acid? To answer this question, the following calculations are performed for the copolymers, AM-4VP-9 and AM-4VP-24.

- **For the AM-4VP-9 copolymer**

The larger of the plateau (area II) correspond to  $\Delta V = 5 \text{ mL}$

The initial copolymer mass is 0.025g.

4VP weight percentage in the copolymer is 8.5% obtained by  $^1\text{H}$  NMR (Table 3).

$$m_{4VP} = 0,025 \times 8,5 \% = 0,002 \text{ g} ; n_{4VP} = 2 \times 10^{-5} \text{ mol}$$

$$\text{and } m_{AM} = 0,025 \times 91,5 \% = 0,023 \text{ g} ; n_{AM} = 3,22 \times 10^{-4} \text{ mol}$$

The necessary volume of  $\text{HCl } 10^{-2} \text{ M}$  solution for the quaternisation of the all 4VP existing in the copolymer is 2 mL. ( $n = C \times V$ ;  $V = 2 \text{ ml}$  or with  $\alpha = [\text{HCl}]/[4VP] = 1$ ).

Calculate the hydrolysis rate of acrylamide in the copolymer

$$n_{AA} = (V_2 - V_1) \times 10^{-3} \times C_{\text{HCl}}$$

$$n_{AA} = 5 \times 10^{-3} \times 10^{-2}$$

$$n_{AA} = 5 \times 10^{-5} \text{ mol}$$

$$n_{AM} = \frac{m - (M_{AA} \times n_{AA})}{M_{AM}}$$

$$n_{AM} = \frac{0,023 - (72 \times 5 \times 10^{-5})}{71}$$

$$n_{AM} = 2,72 \times 10^{-4} \text{ mole}$$

$$\%_{AA} = \frac{n_{AA}}{n_T}$$

$$\%_{AA} = \frac{5 \times 10^{-5}}{2,72 \times 10^{-4} + 5 \times 10^{-5}}$$

$$\%_{AA} = 15,5\%$$

The hydrolysis rate in this case is 15.5 % Based on the obtained result, we can suppose that the plateau (area II) is connected to the hydrolysis of acrylamide and not to a quaternisation of 4VP. To verify this supposition, we will perform the same calculation with the second copolymer

- **For the AM-4VP-24 copolymer**

The larger of the plateau (area II) correspond to  $\Delta V = 1.5 \text{ mL}$

The initial copolymer mass is 0.025g.

4VP weight percentage in the copolymer is 24% obtained by  $^1\text{H}$  NMR (table 3).

$$m_{4VP} = 0,025 \times 24 \% = 0,006 \text{ g} ; n_{4VP} = 5,7 \times 10^{-5} \text{ mol}$$

$$\text{and } m_{AM} = 0,025 \times 76 \% = 0,019 \text{ g} ; n_{AM} = 2,68 \times 10^{-4} \text{ mole}$$

The necessary volume of  $\text{HCl } 10^{-2} \text{ M}$  solution for the quaternisation of the all 4VP existing in the copolymer is 5.7 mL. ( $n = C \times V$ ;  $V = 5,7 \text{ ml}$  or with  $\alpha = [\text{HCl}]/[4VP] = 1$ ).

Calculate the hydrolysis rate of acrylamide in the copolymer

$$n_{AA} = (V_2 - V_1) \times 10^{-3} \times C_{\text{HCl}}$$

$$n_{AA} = 1,5 \times 10^{-3} \times 10^{-2}$$

$$n_{AA} = 1,5 \times 10^{-5} \text{ mole}$$

$$n_{AM} = \frac{m - (M_{AA} \times n_{AA})}{M_{AM}}$$

$$n_{AM} = \frac{0,019 - (72 \times 1,5 \times 10^{-5})}{71}$$

$$n_{AM} = 2,52 \times 10^{-4} \text{ mole}$$

$$\%_{AA} = \frac{n_{AA}}{n_T} \qquad \%_{AA} = \frac{1,5 \times 10^{-5}}{2,52 \times 10^{-4} + 1,5 \times 10^{-5}} \qquad \%_{AA} = 5,6\%$$

The hydrolysis rate in this case is 5,6 %. This result confirm the first supposition

By comparing the AM-4VP-9 and AM-4VP-24 results we can deduce

- The plateau is not connected to a quaternization of 4VP but it's connected to the hydrolysis of acrylamide.
- In both cases the hydrolysis rate of acrylamide is low.

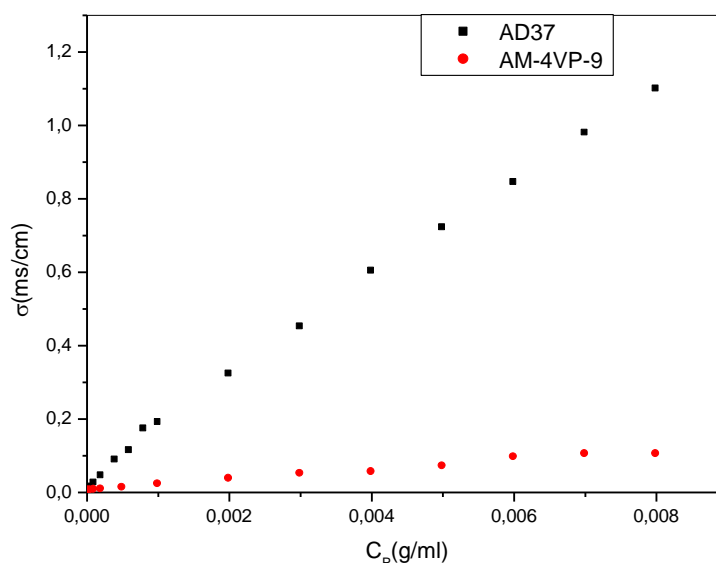
The weight percentages of the two copolymers are summarized in Table 4.

**Table 4:** Weight percentages of constituents of copolymers

| Copolymers | Initial w/w% of AM/4VP | Final w% of AM | Final w% of AA and acrylate | Final w% of 4VP |
|------------|------------------------|----------------|-----------------------------|-----------------|
| AM-4VP-9   | 93,3 / 6,7             | 76,0           | 15,5                        | 8,5             |
| AM-4VP-24  | 66,7/33,3              | 70,4           | 5,6                         | 24              |

### 3.2. Conductivity of copolymers

In this party of this study we will compare the conductivity of our copolymer (AM-4VP-9) with another copolymer we know its charges rate which is the partially hydrolyzed polyacrylamide (AD37 copolymer) [28]..



**Figure 2:** Variation of the conductivity of the copolymers according to its concentration at 25°C

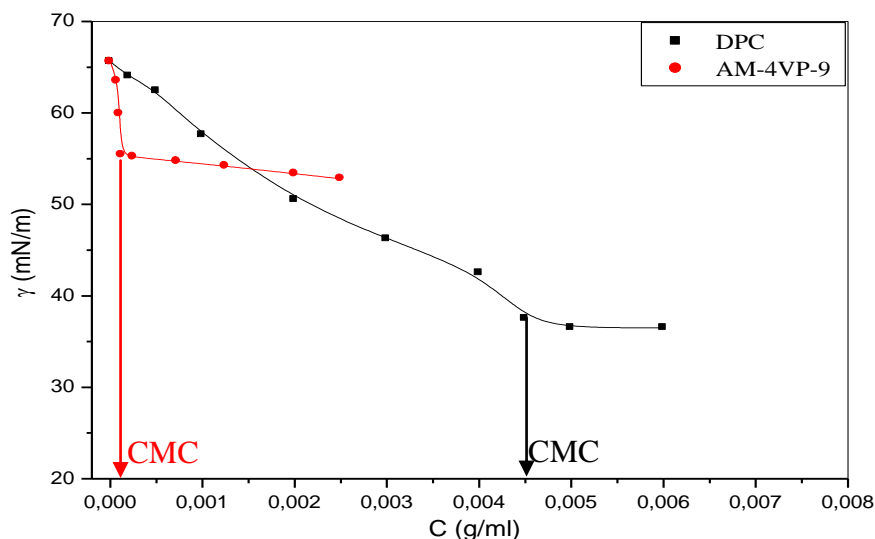
### 3.3. Surfactant properties of AM-4VP-9 copolymer

One of the characteristic properties of surfactants is their tendency to self-associate in solution or in the interface. This leads to their micellization in aqueous solution and in the formation of the films on the liquid/air interface and solid/liquid. Many processes we encounter on a daily basis can be devoted to the knowledge of the properties of adsorption. This comes of the adsorption of surfactant as a main part of several applications such as cleaning, detergent, dispersion, flotation, and lubrication [29-31]. Polymers are likely to develop in the presence of water of the intramolecular associations which lead to the formation of hydrophobic micro-domains. In this party of article, we are interested to study the wide behavior of the AM-4VP-9 copolymer, by comparing it with that of the famous N-dodecyl pyridinium chloride surfactant (DPC).



### 3.3.1. Surfactant properties of AM-4VP-9 copolymer

Fig.3 shows the variation of the surface tension of the copolymer AM-4VP-9 and the N-dodecyl pyridinium chloride (DPC) surfactant as a function of its concentration in aqueous solution at  $T = 25\text{ }^{\circ}\text{C}$ .



**Figure 3:** Variation of the surface tension of the AM-4VP-9 copolymer and the DPC surfactant depending on its concentration in aqueous solution at  $25\text{ }^{\circ}\text{C}$

The shape of the curve of the copolymer is similar to that of surfactant. In the range of concentration  $[0-1,3 \times 10^{-4} \text{ g/ml}]$ , we note a fall decrease in surface tension. Beyond this copolymer concentration ( $C_p = 1,3 \cdot 10^{-4} \text{ g/ml}$ ), the decrease in tension surface becomes low (constant). We can explain this by the adsorption of hydrophobic chains at the water/air interface. Above the concentration ( $C_p = 1,3 \cdot 10^{-4} \text{ g/ml}$ ), we are witnessing the formation of micelles after saturation of the interface. This concentration is called critical micellar concentration CMC. It is in good agreement with the results of the literature, the CMC of polymers takes values in this interval ( $10^{-9} \leq \text{CMC} \leq 10^{-4} \text{ g/ml}$ ) [32].

For this effect, we can say that our copolymer has a power to minimize the water surface tension. This suggests that the copolymer has a character of a surfactant. In our case the copolymer manifests a surfactant character ( $\Delta\gamma = 8 \text{ mN/m}$ ). On the experimental, we note if the copolymer concentration increases the amount of foam increases and persists. Indeed, after the CMC the decrease in surface tension continuous contrary to the surfactant molecules (their surface tensions remain constant after the CMC) [32]). Comparing the curve of the copolymer with a simple surfactant which is the chloride N-dodecyl pyridinium (DPC), we note that the CMC value of the surfactant is  $0.0045 \text{ g/ml}$ . It is in good agreement with our results obtained from viscosity and conductivity [28] and the results of the literature [33, 34]. It is relatively higher than the copolymer CMC. It also notes that the reduction of the surface tension of the copolymer is low compared to the simple surfactant.

### 3.3.2. The relation between the surface tension and $\alpha$

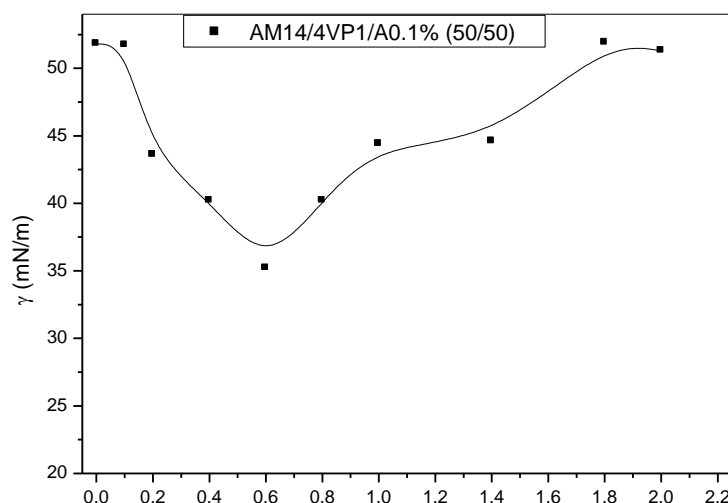
Fig. 4 represent the variation of the surface tension of the AM-4VP-9 copolymer as a function of degree of neutralization  $\alpha$ , for a fixed concentration of copolymer  $C_p = 2,5 \times 10^{-3} \text{ g/ml}$ , knowing that  $\alpha = \text{HCl} / [4\text{VP}]$ . the curve has two ranges of variation, depending on  $\alpha$  values.

#### • $0 \leq \alpha \leq 0.6$

A decrease in surface tension which can be explained, at the beginning for  $\alpha = 0$ , the value of surface tension is that of water. The increase in  $\alpha$  values causes firstly protonation of carboxylate functions ( $\text{RCOO}^-$ ) by  $\text{H}^+$  ions (present in



HCl acid) to form RCOOH insoluble in water which is added to the hydrophobic effect of the 4-vinylpyridine present in the copolymer. The copolymer migrates to the surface water/air (adsorption) which causes a decrease of the surface tension of the water. For  $\alpha = 0.6$ , the surface tension is minimum, it means that the adsorption of the copolymer is maximum.



**Figure 4:** Variation of the surface tension of the AM-4VP-9 copolymer as a function of degree of neutralization  $\alpha$ , for a fixed concentration of copolymer  $C_p = 2,5 \times 10^{-3}$  g/ml, at 25°C

#### • $0.6 < \alpha < 2$

In this region, surface tension increases with  $\alpha$  because of the increased in  $\alpha$  values causes in this case the quaternization of 4-vinylpyridine present in the copolymer by  $H^+$  ions. The obtained copolymer will be quaternised, loaded and soluble in water. The copolymer migrates towards the inside of the water (desorption) what causes an increase in the surface tension to reach that of the water for  $\alpha \geq 1.8$ .

## Conclusion

The conductivity results show that this method of copolymerization leads to hydrolysis of amines functions of acrylamide with a low percentage. This phenomenon is linked to the percentage of acrylamide in the copolymer. In general, the obtained copolymers are weakly charged. Indeed, the Tentiometry results show that the AM-4VP-9 copolymer has a remarkable surfactant character. The degree of neutralization  $\alpha$  has influence on the nature of surfactant copolymer. The surface tension of the aqueous solution of the copolymer depends on the value of  $\alpha$ . The copolymer contains the carboxylates functions ( $RCOO^-$ ). This result confirms the results obtained by conductimetric previously.

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