

p-ANISIDINE RELEASE STUDY BY HYDROLYSIS OF SCHIFF BASES IN HOMOGENEOUS MEDIA

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ABSTRACT. The objective of this work is to study the release of *p*-anisidine by the hydrolysis of synthesized Schiff bases N-vinylbenzylidene-*p*-anisidine (Im) as a monomer and its copolymers (Cp₁, Cp₂) with N,N-dimethylacrylamide (DMA). The hydrolysis behavior and kinetics are investigated in homogeneous media composed of ethanol/water (80% v/v) at 37 °C and at pH range of 4.0-10.0. The variation of the concentration over time is measured in thermostatically cells using UV-Vis spectroscopy. The results showed that the imine function hydrolysis obeyed to the first order for all compounds; the experimental kinetic constants are determined and the pH–rate diagram profile is established. It is noticed that the hydrolysis of imine function is extremely dependent on its carrier and the pH medium.

KEY WORDS: *p*-Anisidine, Copolymer, Schiff base, Hydrolysis, pH–rate diagram, Controlled release

INTRODUCTION

Imine is sometimes called a Schiff base, its formation and hydrolysis have been developed by Patai [1]. These compounds are highly interesting in biological chemistry [2-5] and in biomedical fields, the Schiff base-linked protein and polypeptide hydrogels are very interesting [6]. Schiff bases are also known for their corrosion inhibition efficiency for steel in acidic solution [7] and a variety of active molecules have been grafted using Schiff base link [8-11]. As well, the mechanism of Schiff base synthesis is tracked [12] and the effect of substitutes on Schiff bases' hydrolysis and kinetics has been largely studied [13, 14]. However, the present research is focused on the influence of structural parameters of aromatic polymeric backbone on the hydrolysis of Schiff bases which can provides supplementary data related to the chemical behavior of the imine function in aqueous media.

The first work carried out in homogeneous buffered medium is from Kamogawa *et al.* [15], their results showed that the hydrolysis of Schiff bases monomers derived from (*m,p*)-vinilbenzaldehyde or (*m,p*)-aminostyrene is more rapid than their copolymers with N-vinyl-2-pyrrolidone (VP).

Earlier works have introduced the catalytic effect of acids and bases on the hydrolysis of N-(*m,p*)-vinylbenzylidene-*p*-anisidine and its copolymer with N-vinyl-2-pyrrolidone at different incorporation rates in different pH of homogeneous buffered and hydro-ethanolic media [16].

It has been found that *p*-anisidine (4-methoxyaniline) is a new $\Delta 6$ desaturation inhibitor, for *Mortierella alpina* strains [17]. In this work, as an active ingredient, *p*-anisidine is grafted on monomer and copolymers using imine link to get new controlled formulations which can release

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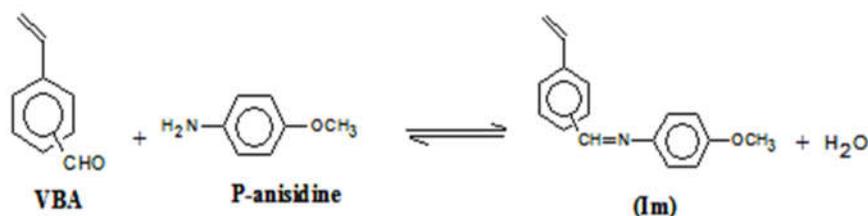
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it progressively. So, in our previous study [18], *N*-(*m,p*)-vinylbenzylidene-*p*-anisidine Schiff base was synthesized and copolymerized with *N,N*-dimethyl-acrylamide (DMA) at two molecular ratios, where the hydrolysis of imine function was studied only in acidic homogeneous and heterogeneous media at pH = 4.7 and 4, respectively [18]. Hence, the present paper is devoted to the study of the hydrolysis kinetics of these new *p*-anisidine based monomer and copolymers in homogeneous media at different pH; the work is intended to identify and discuss the hydrolysis mechanism in one hand and in the other hand to determine the effect of copolymerization on the hydrolysis constant. So, using these different carriers, i.e. monomer and copolymers, the *p*-anisidine release and hydrolysis can be modified and controlled over time.

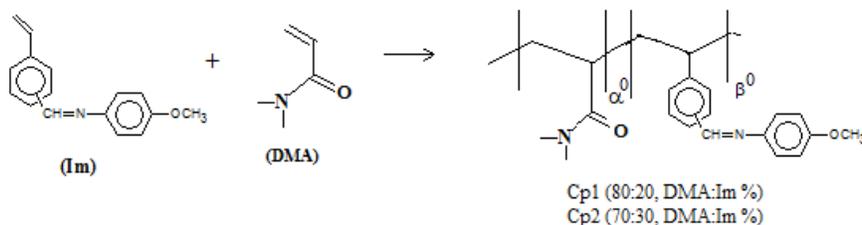
EXPERIMENTAL

Preparation and characterization of monomer and copolymers

The monomer *N*-(*m,p*)-vinylbenzylidene-*p*-anisidine (Im) and its copolymers with *N,N*-dimethylacrylamide Cp₁ and Cp₂ (Schemes 1 and 2, respectively) are synthesized according to the experimental method described in our previous research [18].



Scheme 1. Global reaction of Schiff base synthesis.



Scheme 2. Copolymerization reaction of *N*-(*m,p*)-vinylbenzylidene-*p*-anisidine with *N,N*-dimethyl-acrylamide.

As described previously [18], the results of monomer (Im) characterization is as following: FTIR spectroscopy (cm^{-1}) revealed the following characteristic bands: 2837.1-2916.2 (C-H), 1622.0 (C=N), 1604.7 (C=C aromatic), 1247.9-1290.3 (C-O), 991.3-906.5 (C-H vinylic). ^1H NMR displayed the peaks at δ (ppm): 5.35-6.00 (2d, $\text{CH}_2=\text{CH}-$), 8.62 (s, $\text{CH}=\text{N}-$), 6.78-6.85 (2d, $\text{CH}_2=\text{CH}-$), 3.8 (s, OCH_3), 6.96-7.90 (8H of 2 phenyl). Microanalysis of the Schiff base monomer $\text{C}_{16}\text{H}_{15}\text{ON}$ ($237.16 \text{ g. mol}^{-1}$) gave the experimental % of C (80.96%), H (6.32%) and N (5.90%). As well, copolymers (Cp₁) and (Cp₂) are characterized by FTIR spectroscopy, GPC, DSC and microanalysis [18]. The values of incorporation ratios (α^0 , β^0) are determined from the microanalysis results. The copolymers' characteristics [18] are displayed in Table 1 and showed that the molecular weight of copolymer Cp₁ is higher than of Cp₂, so using a high percentage of

DMA induced a high copolymer weight. However, the incorporation ratio (β^0) of imine in Cp₂ is increased indicating a high Schiff base content. Practically, the FTIR characteristic bands of Cp₁ and Cp₂ appeared in same regions.

Table 1. Characterization results of copolymers.

| | FTIR bands (cm ⁻¹) | Molecular weight | Tg (°C) | Incorporation ratios ($\alpha^0_{DMA}/\beta^0_{Im}$) |
|-----------------|---|---|---------|---|
| Cp ₁ | 2852.5-2925.8 (C-H) 1649.0 (C=O) 1624.0 (C=N) 1245.9 (C _{aro} -O) | $M_n = 20600$ $M_p = 26500$ $I = 1.3$ | 218 | $\alpha^0 = 0.65$, $\beta^0 = 0.35$ ($\alpha^0_{DMA}/\beta^0_{Im} = 1.857$) |
| Cp ₂ | 2850.6-2922.0 (C-H) 1649.0 (C=O) 1624.0 (C=N) 1244.0 (C _{aro} -O) | $M_n = 10500$ $M_p = 13100$ $I = 1.2$ | 146 | $\alpha^0 = 0.52$, $\beta^0 = 0.48$ ($\alpha^0_{DMA}/\beta^0_{Im} = 1.083$) |

Hydrolysis kinetics and UV-Vis analysis

The hydrolysis kinetics of Schiff bases monomer (Im) and copolymers (Cp₁) and (Cp₂) are studied at a temperature of 37±0.1 °C using an UV-Vis spectrophotometer (Shimadzu UV-2401 PC; Tokyo, Japan) equipped with thermostatically cells. The kinetics are conducted in homogeneous media composed of buffer solutions which are prepared in 80:20 ethanol/water (v:v) where the ionic strength is maintained at 0.01 and the pH range varied from 4.0 to 10.0.

The buffer solutions are prepared according to the methods described by Perrin [19], Michaelis-Mizutani [20] and Bates *et al.* [21] where water is substituted by a mixture of ethanol:water at 80:20 (v:v). A Tacussel digital pH meter is used for the pH measurements in cells.

For hydrolysis study procedure, the UV-Vis reference cell contained 2.70 mL of buffer solution (in 80:20 of ethanol:water), 0.06 mL of double distilled water and 0.24 mL of ethanol. However, the analysis cell contained 2.70 mL of buffer solution (in 80:20 of ethanol:water), 0.06 mL of double distilled water and 0.24 mL of 10⁻³ M ethanolic solution of a monomer (Im) or a copolymer (Cp₁ or Cp₂). The total volume of liquid in cell is maintained at 3 mL. In these conditions, the initial concentration of all compounds in the analysis cell is kept at 8 x 10⁻⁵ M. The molar masses of copolymers (M_{Cp}) are calculated on the basis of the repeating unit or pattern in copolymer according to the following equation:

$$M_{Cp} = \alpha^0 \cdot M_{DMA} + \beta^0 \cdot M_{Im} \quad (1)$$

where M_{DMA} and M_{Im} are molar masses of dimethylacrylamide (DMA) and vinylbenzylidene-p-anisidine (Im), respectively.

RESULTS AND DISCUSSION

Hydrolysis study of monomer and copolymers Schiff bases

The UV-Vis spectra of Schiff bases have been described by many authors and particularly by El-Bayoumi *et al.* and Belletête *et al.* [22, 23]. This type of compounds have 4 bands (I to IV) which the first and the second one (I and II) correspond to n→π* transition and appear at wavelengths different from those of aldehydes. These four bands (I to IV) appear clearly in the UV-Vis spectrum of the monomer N-(m,p)-vinylbenzylidene-p-anisidine in ethanol and remain unchanged in the initial time (t₁) of Im hydrolysis in the hydro-ethanolic study medium as shown in Figure 1a. Full

UV spectra are registered for slow kinetics. An example is given in Figure 1a for Im hydrolysis at pH = 6.18; the UV spectra are registered at different times during the hydrolysis process.

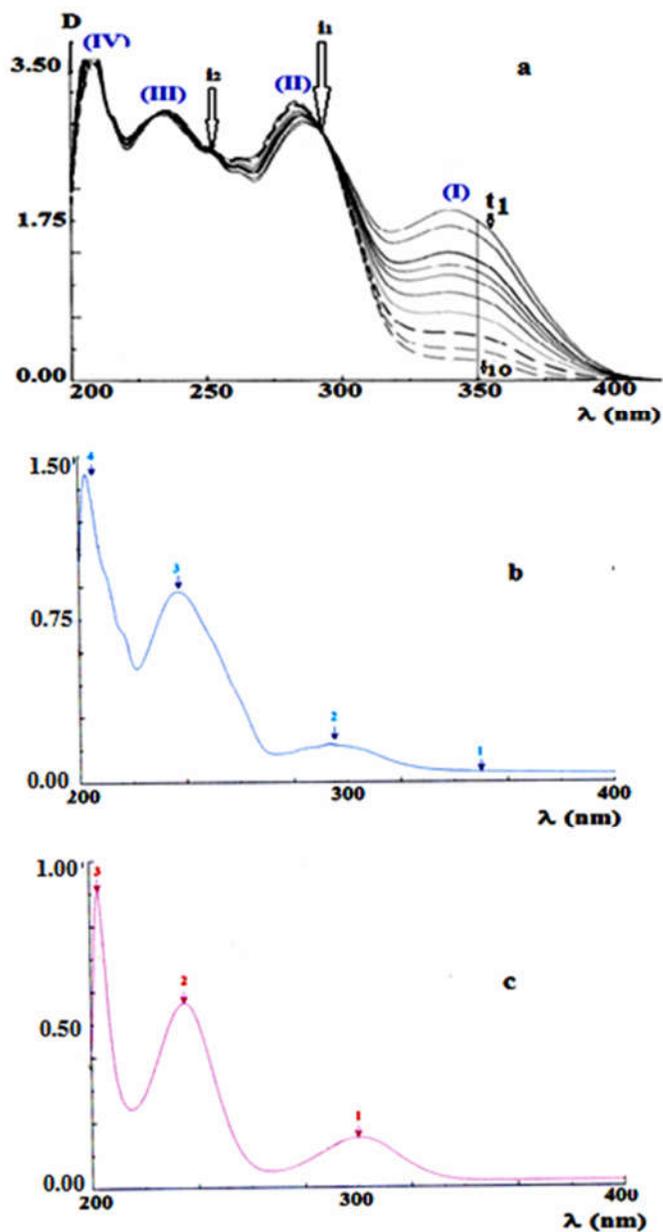
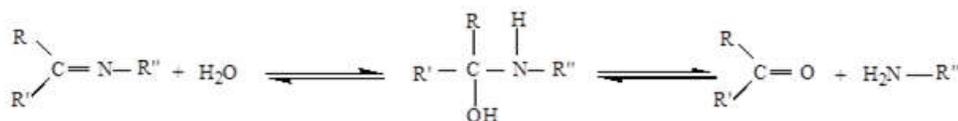


Figure 1. UV spectra registered at pH = 6.18; a: Im, b: *(m,p)*-vinylbenzaldehyde c: *p*-anisidine.

The comparison of UV spectra of Im (Figure 1a) and *p*-aniside (Figure 1c) and *m,p*-vinylbenzaldehyde (Figure 1b) in same conditions revealed that the band I which corresponds to $n \rightarrow \pi^*$ transition of imine function is the most appropriate to keep track the hydrolysis kinetic. It is observed that its intensity diminishes during the hydrolysis process indicating the imine function destruction.

Figure 2 showed the UV spectra of Cp₂ hydrolysis at pH = 6.18, the first spectrum (n°1) which is registered at time < 30 s displayed also four bands at 334, 266, 240 and 212 nm attributed to an aromatic Schiff base, that is the copolymer Cp₂ before hydrolysis. In this case, also the band (I) is chosen for the imine constant hydrolysis determination. In the last spectrum (n°10), it is observed that the band (I) disappeared indicating completion of hydrolysis and obtaining the two spectra of amine and aldehyde (Scheme 3).

The presence of isobestic points “i₁” and “i₂” as mentioned in Figure 1a and 2 indicates that there was no accumulation of any intermediate, especially the α -amino alcohol, during the hydrolysis process both of imine (Im) and copolymers (Cp₁) and (Cp₂) (Scheme 3).



Scheme 3. Schiff base hydrolysis.

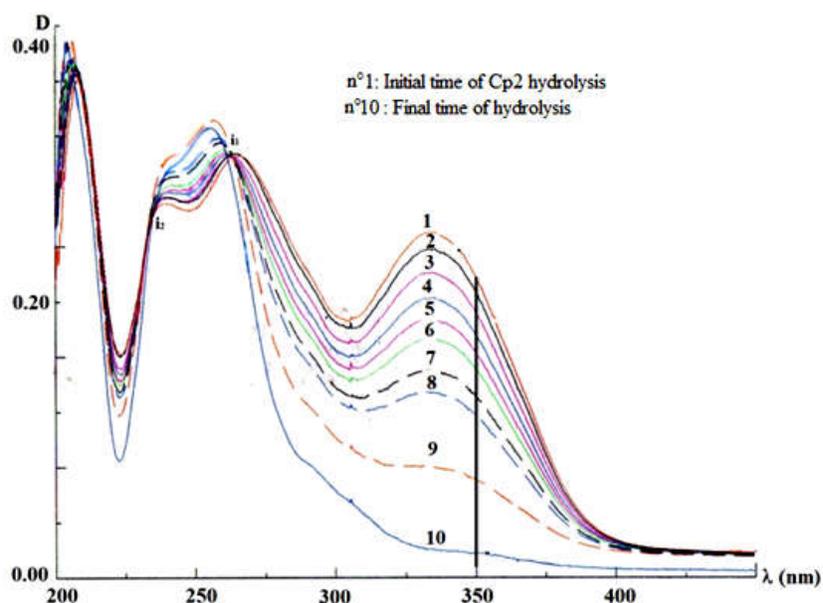


Figure 2. UV spectra of Cp₂ at different time of hydrolysis at pH = 6.18.

For pH values less than 5, the hydrolysis process is more rapid; in this case, another method is used to track the hydrolysis kinetic. In fact, a quantitative method of the UV apparatus is used, the analytical wavelength is set at 350 nm (band I), and the optical density (D) is displayed as a function of time as shown in Figure 3 for Im hydrolysis in pH medium equal to 4.65.

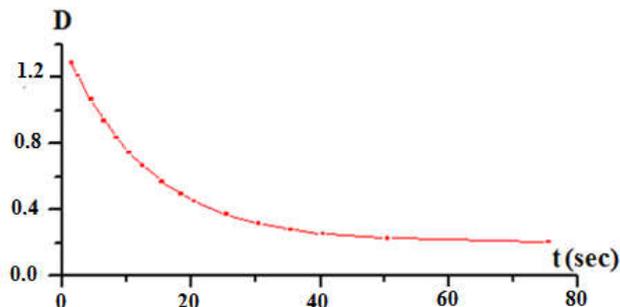


Figure 3. UV Kinetic curve of Im hydrolysis at pH = 4.65, $D = f(t)$ measured at $\lambda = 350$ nm.

If the hydrolysis kinetic is considered as a first-order reaction, it obeyed to the equation 2:

$$\text{Log } D_{\lambda} = \log D_{\lambda}^0 - \frac{k_{obs}}{2.3} t \quad (2)$$

where D_{λ} and D_{λ}^0 are corrected optical density at time t and initial optical density both are measured at the wavelength λ , k_{obs} is a hydrolysis constant. The corrected optical density D_{λ} is equal to actual optical density minus the measured optical density at infinite time.

On one hand, the experimental data are plotted and linear fits of $\log(D_{\lambda}) = f(t)$ for imine (Im) and copolymers (Cp₁ and Cp₂) at pH 4.16, 6.18, 7.71 and 9.91 are obtained. Examples of fits are given in Figure 4. Consequently, the hydrolysis kinetics of these Schiff bases in ethanol buffer mixtures are considered as first-order reactions.

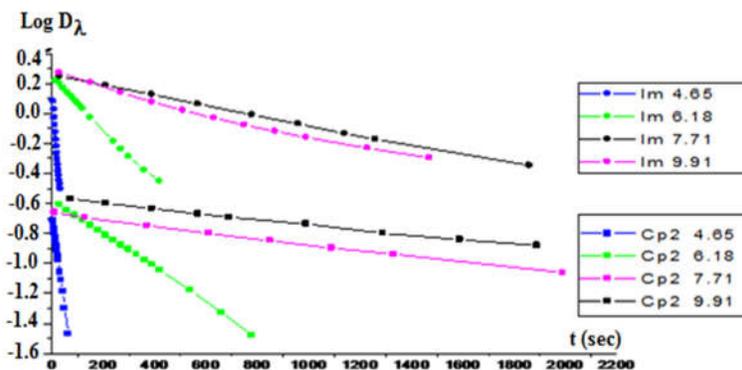


Figure 4. Plots of $\log(D_{\lambda})$ as a function of time for monomer and copolymer Cp₂ hydrolysis at different pH values.

On the other hand, the initial optical densities read at $\lambda = 350$ nm from the linear plots of $\log(D_{\lambda}) = f(t)$ checked the Lambert-Beer law, as noticed in Table 2, at different concentrations of imine (Im), experimental hydrolysis constant (k_{obs}), half reaction time ($t_{1/2}$) and initial optical density (D^0) are measured and a linear plot of $D^0_{\lambda} = f(C)$ is obtained as shown in Figure 5. The first order is also confirmed by the quasi-constancy of $t_{1/2}$ whatever the initial concentration C_0 of the free imine (Im) or copolymer carriers (Cp).

Table 2. Confirmation of the first order by checking Lambert-Beer law for imine Im.

| | | | | | |
|---------------------------------------|------|------|------|-------|-------|
| $C_0 \times 10^4 \text{ M}$ | 1 | 0.8 | 0.6 | 0.4 | 0.2 |
| $k_{obs} \times 10^4 (\text{s}^{-1})$ | 53.6 | 50.4 | 50.1 | 52.4 | 54.5 |
| $t_{1/2} (\text{s})$ | 129 | 137 | 138 | 132 | 127 |
| D_{350}^0 | 1.67 | 1.32 | 1.04 | 0.643 | 0.341 |

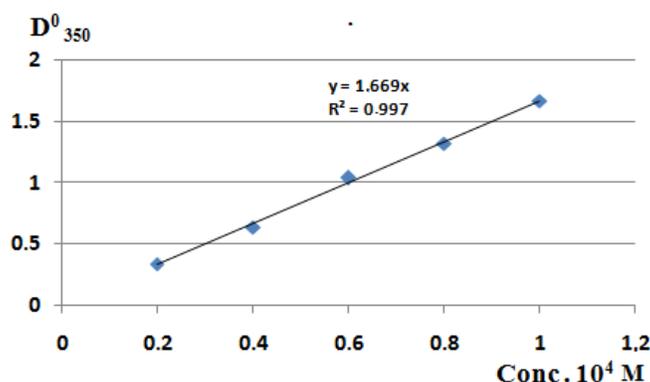


Figure 5. A linear plot of $\log(D^0_{350}) = f(C)$ of Im for Lambert-Beer law verification.

Then, experimental kinetic constants (k_{obs}) of all compounds and at four values of pH are calculated from the slope of the $\log(D_\lambda) = f(t)$ curve and the initial optical density D_λ^0 is determined by extrapolation at $t = 0$. The corresponding results are given in Table 3.

Table 3. Hydrolysis kinetic parameters of Im, Cp₁ and Cp₂.

| pH | (Im) | | (Cp ₁) | | (Cp ₂) | | $\frac{k_{Im}}{k_{Cp1}}$ | $\frac{k_{Im}}{k_{Cp2}}$ |
|------|---------------------------------|-------|---------------------------------|-------|---------------------------------|-------|--------------------------|--------------------------|
| | | | $Mn = 20600, \beta^0 = 35\%$ | | $Mn = 10500, \beta^0 = 48\%$ | | | |
| | $k \times 10^4 (\text{s}^{-1})$ | D^0 | $k \times 10^4 (\text{s}^{-1})$ | D^0 | $k \times 10^4 (\text{s}^{-1})$ | D^0 | | |
| 4.65 | 790 | 1.62 | 455 | 0.10 | 294 | 0.22 | 1.74 | 2.68 |
| 6.18 | 53.0 | 1.66 | 52.0 | 0.14 | 26.2 | 0.26 | 1.02 | 2.02 |
| 7.71 | 9.60 | 1.68 | 5.84 | 0.22 | 3.50 | 0.19 | 1.64 | 2.74 |
| 9.91 | 11.0 | 1.50 | 8.00 | 0.16 | 3.97 | 0.27 | 1.38 | 2.77 |

It is noted that by varying the pH medium, D^0 is almost constant for each compound; in fact, the mean value of D^0 are respectively 1.615 for Im, 0.155 for Cp₁ ($\beta^0 = 35\%$) and 0.235 for Cp₂ ($\beta^0 = 48\%$). It is coherent that D^0 at $\lambda = 350 \text{ nm}$ of copolymers should be lower than D^0 of Im since the concentration of imine group in copolymers depends on the degree of incorporation (β^0). In fact, at initial time, the imine concentration in copolymer is significantly lower than pure imine. Also, by comparing Cp₁ and Cp₂, the value of D^0 is in agreement with copolymers' imine content, so higher is the incorporation rate (β^0), higher is the initial optical density (D^0). The results showed obviously that at same pH value, the hydrolysis constants of copolymers (Cp₁, Cp₂) are lower than of the monomer (Im). It is noticed that the carrier, i.e. copolymer backbone affects significantly the hydrolysis constant. As a result, copolymers and especially Cp₂ exhibited delayed *p*-anisidine release since the hydrolysis constant is decreased.

derived from aromatic and aliphatic amines can be divided into different zones [13]. In Figure 6, two zones of hydrolysis called A and P appeared that are meaning acidic zone catalysis and basic plateau, respectively. Between 4.65 and 7.71 of pH value corresponding to a zone A, the hydrolysis reaction is catalyzed by acidity since the observed hydrolysis constant decreases noticeably when pH increases. In these conditions, it is considered that the protonated imine is attacked by water molecules but the values of the slopes of $\log k_{\text{obs}} = f(\text{pH})$ is lower than unity indicating that the base catalysis cannot be neglected [13]. A same shape of curves $\log k_{\text{obs}} = f(\text{pH})$ (Figure 6) is obtained both for the free imine and copolymers that confirmed that the hydrolysis mechanism remains unchanged whatever the imine carrier. Similar results have been noticed for other Schiff bases [24-25].

Also, as reported in previous research [8], the hydrolysis curves of Schiff bases derived from pyrrolic aldehydes gave similar zones from pH = 4 to 12. However, as reported by Barmatov and Hugues [7], for the Schiff base N-(4-(dimethylamino)benzylidene) benzothiazol-2-amine 3; a specific acid catalysis mechanism is observed from pH = 2.76 to 7.51.

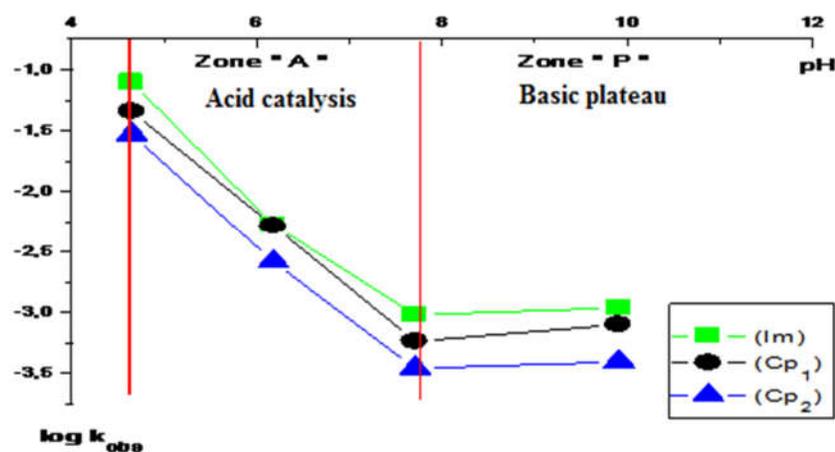


Figure 6. Hydrolysis curves ($\log k_{\text{obs}} = f(\text{pH})$) of compounds (Im), (Cp_1) and (Cp_2).

For Im, Cp_1 and Cp_2 and from pH 7.71 and 9.91 appeared a zone P of basic plateau of the pH-rate curve (Figure 6), in this zone, it is demonstrated that the rate-limiting step corresponded to the nucleophile attack of hydroxide anion on the protonated imine and the kinetic constant is independent from pH [13, 25].

In the two zones of pH, the results showed that the hydrolysis of free imine (Im) is more rapid than copolymers Cp_1 and Cp_2 . So, the delayed effect due the copolymerization is distinguished. Besides, if we compare the two copolymers, it is seen that the hydrolysis constant k_{obs} of Cp_1 is higher than k_{obs} of Cp_2 whatever the pH value. From the copolymers' characterization, Cp_2 contained more Schiff bases or imine groups ($\beta^0 = 48\%$) and had a low molecular mass (M_n). So, it seems that there is no correlation between the molecular weight M_n and the kinetic constants but rather a specific effect of the close statistical pelota of polymer is occurred. In fact, in Cp_2 , the amide:imine ratio is close to 1:1, intra-molecular and intermolecular interactions can be arise and so the hydrolysis reaction is inhibited and the constant k_{obs} decreased.

The similar hydrolysis curves are obtained for both the free imine and its copolymers (amide-imine), so the hydrolysis mechanism of the imine function remained virtually unchanged regardless of its backbone carrier. As well, same hydrolysis curve profiles of aromatic Schiff base

are obtained by other researchers [13, 24, 26-27]. Finally, it is noticed that the hydrolysis constants of these aromatic Schiff bases (Im and Cp) are higher than those of *p*-anisidine Schiff bases derived from *N*-pyrrolic and *N*-methyl pyrrolic aldehydes [13].

CONCLUSION

The present research discusses the *p*-anisidine controlled release by hydrolysis process of Schiff bases derived from aromatic backbone. The hydrolysis of free imine or *N*-(*m,p*)-vinylbenzylidene-*p*-anisidine (Im) and its copolymers with *N,N*-dimethylacrylamide (Cp₁) and (Cp₂) is studied in pH range of 4 to 10 and using UV-Vis analysis. The experimental results showed that the mechanism of hydrolysis reaction is a pseudo first order. The experimental kinetic constants are calculated and the morphology of the hydrolysis curves $\log k_{\text{obs}} = f(\text{pH})$ confirmed that the hydrolysis mechanism did not undergo any modification when moving from the free mono-imine molecule (Im) to the polymer carrier; in this range of pH, two zones namely A and P are obtained. Whatever the pH, the hydrolysis kinetic constant (k_{obs}) of mono-imine is higher than those of copolymers. However, for copolymers, it is observed that the k_{obs} decreased when the degree of imine incorporation increased. Finally, the copolymer Cp₂ displayed a slow hydrolysis and a delayed *p*-anisidine release.

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