Acid–Base Behavior of an Oligomer of 3-Amino-1,2,4-triazole

Melisa E. Lamanna,[1] Enrique de la Horra,[2] Juan Sanabria,[2]
Silvia E. Jacobo,[2] Norma B. D'Accorso[1]

[1]Centro de Investigaciones en Hidratos de Carbono (CIHIDECAR-CONICET), Dpto. de Química Orgánica,
Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Ciudad de Buenos Aires (1428),
Buenos Aires, Argentina
[2]Laboratorio de Físico Química de Materiales Cerámicos Electrónicos (INTECIN -CONICET), Dpto. de Química,
Facultad de Ingeniería, Universidad de Buenos Aires, Buenos Aires, Argentina

ABSTRACT: We report the acid–base behavior of OATA, an oligomer synthesized from 3-amino-1,2,4-triazole (ATA). We analyze the UV–vis spectroscopy at different media, and we analyze and discuss the acid–base equilibria taking into account tautomeric equilibria at different pH. The low aqueous solubility at neutral pH can be attributed to the neutral form. Indeed, OATA was synthesized in an ordinary filter paper, which can be used as a sensor for ammonia as well as endpoint indication. Using the OATA-containing paper, ammonia concentrations in a solution as low as 5 ppm could be measured. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 123: 2768–2774, 2012

Key words: oligo-3-amino-1,2,4-triazole; endpoint indicator; characterization; tautomeric equilibria; filter paper; UV–vis

INTRODUCTION

1,2,4-Triazoles represent a class of heterocyclic compounds with significant importance in agriculture and medicine.[1] Particularly, 1,2,4-triazoles substituted are among the various heterocycles that have received the most attention during the last two decades as potential antimicrobial agents.[2–6] They are also used in metallo-organic chemistry as polyfunctional ligands.[7]

We have previously performed the polymerization of 3-amino-1,2,4-triazole (ATA), an insulator material, in acidic aqueous solution with ammonium persulfate (APS) as initiator. The oligomer of ATA (OATA) is precipitated, within few hours, after neutralization. The new material, conveniently doped, turned out to be a semiconductor tetramer, and it showed higher thermal stability than the corresponding monomer. We have also observed that the products at various stages of OATA polymerization showed visible color changes.[8]

Fibrous cellulose-containing filter papers are useful in filtration; they are inexpensive and easy to produce in different shapes and sizes. Therefore, an ordinary filter paper could be used as the base substrate for fabrication of indicators, sensors, and membranes for filtration of acids and bases with appropriate active materials embedded in it. Dutta et al.[9] synthesized polyaniline (PANI) in an ordinary filter paper, and they showed that a stable PANI-containing filter paper can be made and that it can act as an acid–base sensor and endpoint indicator but also can filter acids and bases.

On the other hand, we also observed that the color and solubility of OATA are strongly pH dependent. In acidic solution, the salt appears light yellow characteristic absorbance at 400 nm, meanwhile at base solution, the color changes to burgundy with characteristic absorbance at around 480 nm. It is logical to assume that the color changes could be a good premise for the development of acid–base sensors.[8]

Moreover, it is necessary to appreciate the tautomerism in five-member heterocyclic systems, which has been recognized for a long time.[10,11] Knowledge of the tautomeric preferences and the factors affecting the equilibrium are essential to understand the compounds reactivity in chemical processes and their effects on biological systems. Because of annular prototropic tautomerism, 1,2,4-triazoles, particularly amino-1,2,4-triazoles without substituents on the ring nitrogen atoms, a priori, can exist in three forms, namely, 3-amino-1H-1,2,4-triazoles (A), 5-
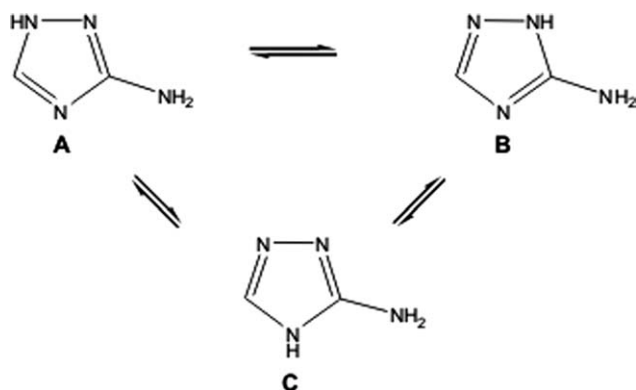
Figure 1 Tautomeric equilibria of ATA.

amino-1H-1,2,4-triazoles (B), and 3-amino-4H-1,2,4-triazoles (C)[12] (Fig. 1).

The aim of this article is to explore the acid–base equilibrium taking into account the corresponding tautomeric species, their correlation with the low aqueous solubility at neutral pH and to investigate the polymerization of ATA in an ordinary filter paper to evaluate the possible application as a sensor and as an acid–base endpoint indicator.

EXPERIMENTAL

Oligomer preparation

All the reagents: ATA, APS, hydrochloride acid (HCl), and ammonium hydroxide (NH$_4$OH) were obtained from commercial suppliers (Aldrich) and used without further purification.

We have successfully polymerized ATA in acidic media, and we have characterized by spectroscopical, thermal, and physical experiments confirming that it is an oligomer with four units.[8] A HCl solution containing ATA was added to an aqueous solution of APS, in the molar relationship 1 : 1.25 at pH 3.0. The reaction mixture was remained at room temperature for 60 min, and the solution was neutralized by NH$_4$OH. The final product precipitated after the solution volume was reduced by evaporation. The solid was filtered, washed several times with water, and dried at vacuum.

Solubility experiments

Standard solutions with pH = 1.5, 5.0, 7.0, 10.0, and 11.6 were prepared from distilled deionized water with HCl or NaOH. Different aliquots of each solution were carefully added at room temperature to a constant mass of OATA (near 60 mg) with constant stirring until a complete dissolution.

Fourier-transform infrared spectroscopy

Fourier transform infrared (FTIR) spectra were recorded on a Nicolet FTIR Instrument 510P. For this purpose, potassium bromide (KBr) and solid oligomer pellets obtained at different pHs were prepared. All experiments in this study were performed at room temperature.

Thermogravimetry analysis

Thermogravimetry analysis (TGA) was performed in a TGA-51 Shimadzu thermogravimetric analyzer. The temperature range was 20–600°C at a heating rate of 5°C min^{-1} with applied nitrogen flux of 40 mL min^{-1}, mass sample of 5–5.5 mg.

Acid–base titrations

The pH response of a basic solution (20 mg OATA dissolved in 30 mL of NaOH 0.01M) was performed with HCl 0.01M. The accurate pH was measured with Oakton digital pH meter.

UV–vis absorption spectra

Spectrophotometric measurements were carried out using a Shimadzu UV-2401 PC spectrometer (spectral range of 200–900 nm) fitted with a 10-mm pathlength quartz cell and equipped with the corresponding software.

Buffer solutions

Standard solutions with pH = 1.4, 2.2, 2.6, 4.0, 4.6, 6.9, 9.0, 10.0, and 12.8 were prepared with traditional procedure from distilled deionized water with HCl, NaOH, H$_3$PO$_4$, KHC$_8$H$_4$O$_4$, KH$_2$PO$_4$, H$_2$B$_4$O$_7$, NaHCO$_3$, KCl, and Na$_2$CO$_3$.

The concentration was 0.1M for acid- and basic-conjugated species. In most cases, the pH will have to be adjusted using a pH meter and the dropwise addition of either 6M HCl or 6M NaOH to 1 L of solution. The accurate pH for each buffer solution was measured with Oakton digital pH meter.

Measurements of color

OATA was dissolved in water to make stock solutions with concentrations of 0.2 mg mL^{-1}, and aliquots of 1.0 mL of these solutions were dissolved in 5.0 mL of each buffer solution to give a final concentration of 0.03 mg mL^{-1}. UV–vis spectra were recorded between 250 and 600 nm. Pure buffers were used as reference cell solutions. For measures reproducibility, each experiment was performed in triplicate.

Preparation of OATA-embedded filter paper

Commercially available Whatman 40 filter papers were cut into about 3-cm diameter circular pieces. Two stock aqueous solutions were prepared, one

TABLE I
OATA Solubility at Different pH Values

pH	1.5	5.0	7.0	10.0	11.6
OATA (mg mL^{-1})	0.60	0.55	0.32	0.83	1.0
λ Máx (nm)	401	425	442	460	473

Maximum λ of UV spectra absorption is indicated.

with 300 mg ATA in 5 mL MilliQ water and the other with 1.824 mg of APS in 5 mL MilliQ water. A quantity of 200 µL of the ATA solution was pored in several drops over the paper using an automatic pipette. Immediately, 200 µL of the APS solution was then added drop by drop, and the paper was allowed to dry in air. The filter paper turns light yellow in 5 min and then orange in 6 h. These papers were cut into a rectangular-shaped piece (1 × 0.5 cm) and were kept hanging in a cylinder flask that contained ammonia solution with different concentrations (5–600 ppm).

RESULTS AND DISCUSSION

Solubility

OATA shows different solubility and different UV spectra profile with the pH. The experimental results are resumed in Table I.

We can observe that the minimum of the solubility corresponds to neutral pH. It is known that molecules, for example, amino acids, have minimum solubility in water or salt solutions at pH, which corresponds to their isoelectric point (pI) and often precipitate out of solution. We can conclude that this lower solubility of the OATA is primarily due to the absence of charge on the structure.

It is necessary to remark that the intermolecular interactions (oligomer–oligomer or oligomer–solvent) are very different in each structure. Charged species have interaction forces much greater than those where only hydrogen bond interactions could be observed.
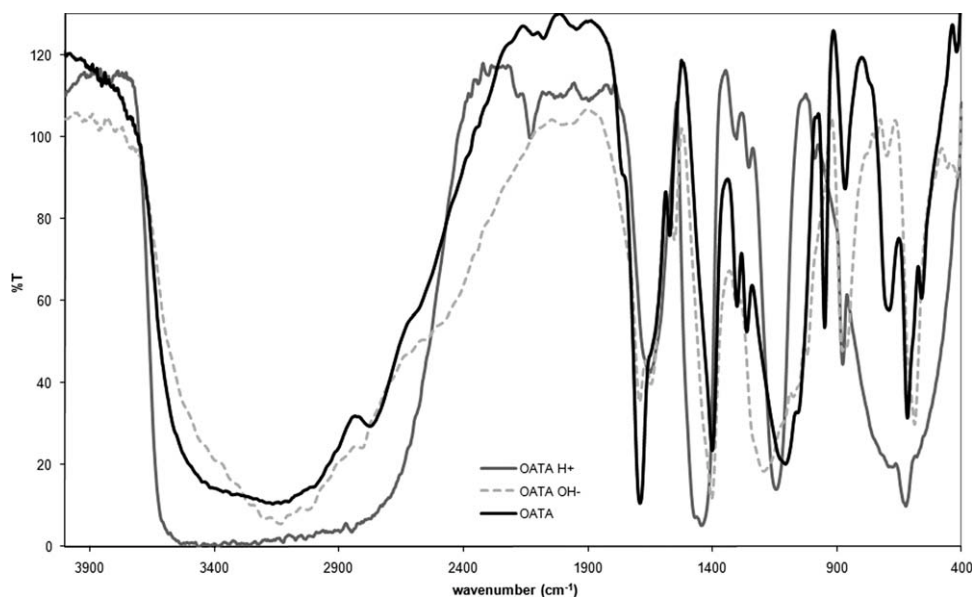
FTIR analysis

As shown in Figure 2, the FTIR spectra of OATA were obtained from samples prepared at different pH values. The absorption peaks at: 3300–3500 cm^{-1} (characteristic of NH and NH$_2$ stretching) in all the cases, bands at 1680–1690 cm^{-1} (corresponding to C=N bond as well as strongly copulated triazole ring stretching and deformation modes);[13] and 1300, 1270 cm^{-1} due to secondary aromatic amines are observed. The absorption peaks at 950, 850 cm^{-1} could be assigned to the C—H out-of-plane bending vibration of the triazole substitution.[14]

It could be observed that the peak at nearly 1600 cm^{-1}, which corresponds to the unsaturated bond, is the most affected with the pH variations. Also, in range 600–700 cm^{-1}, we observed the NH out-of-plane bending.[14] It is interesting to remark that these variations in the FTIR spectra could be consequence of different protonation of the heteroatoms present in the oligomer.

Thermogravimetry analysis

To explore the thermal behavior of this oligomer at different pHs, we carried out the TGA of the samples: OATA (N), OATA (B), and OATA (A) (Fig. 3).

All the samples show thermal decomposition temperature (T_d) between 200 and 300°C. This step results

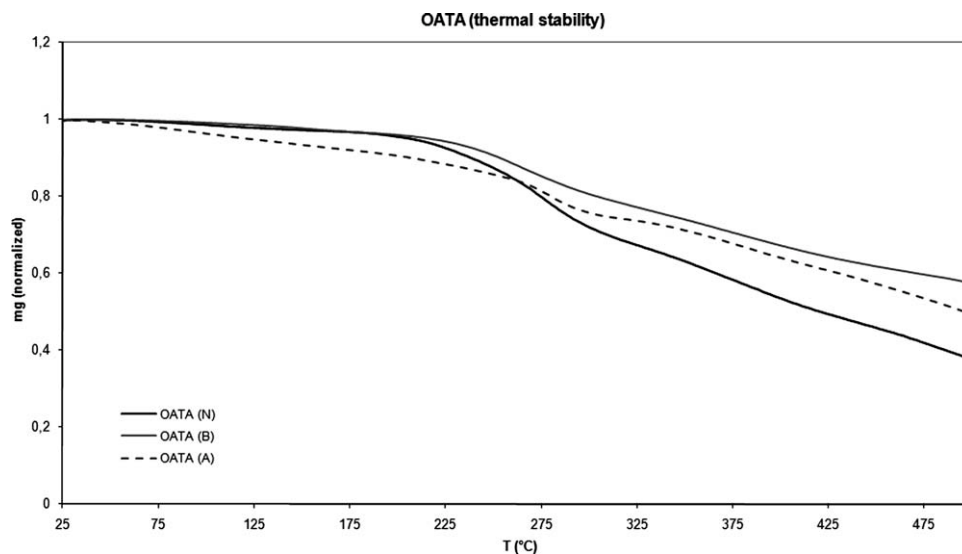**Figure 2** FTIR spectra of OATA species obtained at different pHs.

Figure 3   Thermogravimetric analysis of OATA samples.

in loss of N_2 and cyanhydric acid (HCN) followed by ring cleavage and loss of a further N_2 molecule.[15]

OATA (A) shows a weight loss of 4.5% between 100 and 180°C, which could be attributed to the expulsion of loosely bound water molecules from the polymer chain.

The derivative curve of TGA (DrTGA) was used to determinate the peak temperature involved in each weight loss. From this analysis, OATA (A) showed the highest T_d with the lowest weight loss percentage.

The results obtained from TGA and DrTGA data are resumed in Table II.

Acid–base titrations

Figure 4 shows the pH profile of a basic solution (0.6 mg mL^{-1}) of OATA while small volumes of chloride acid are added. The rows indicate every small change in the curve during titration. These changes are related to acidic constants (k_i) although these constants cannot be determined by this method, probably as they are much closed one of each other. A minimum of the first derivate (Fig. 4) indicates the titration endpoint.

The pH response of OATA shows different behavior during the protonation of the basic structure in comparison with deprotonation of the acidic form and evidence some hysteresis (Fig. 5).

TABLE II
Summary of Thermal Analysis Results for the Studied Samples

	T_d (°C)	% Weight loss (T_d)
OATA (N)	276.5	29.98
OATA (B)	264	18.41
OATA (A)	280	12.03

The results presented here suggest that acid–base titrations should depend on the starting bulk pH condition. During the titrations, solvation reactions may also take place so that can modify the titration curve.

A possible explanation for the observation in Figure 5 is:

- if the OATA is initially solubilized in a basic medium, an interaction between the negatively charged molecules does not occur; therefore, the solvation by the aqueous medium is high so that a large number of molecules can be deprotonated (curve 1).
- When OATA is in acidic medium, an interaction between molecules of OATA that prevents a complete solvation takes place. The interaction with the environment is insufficient, and this
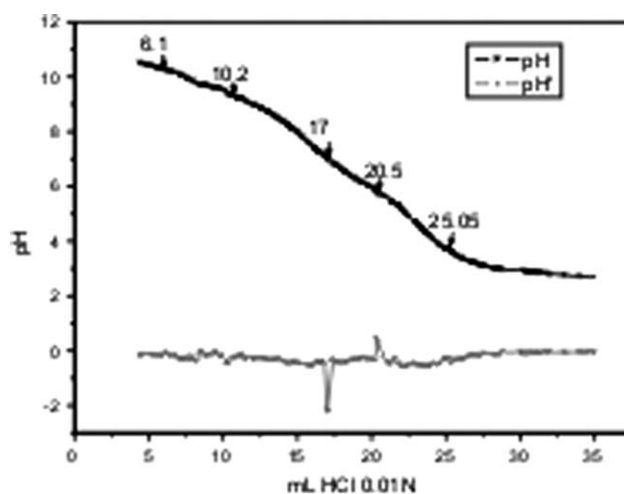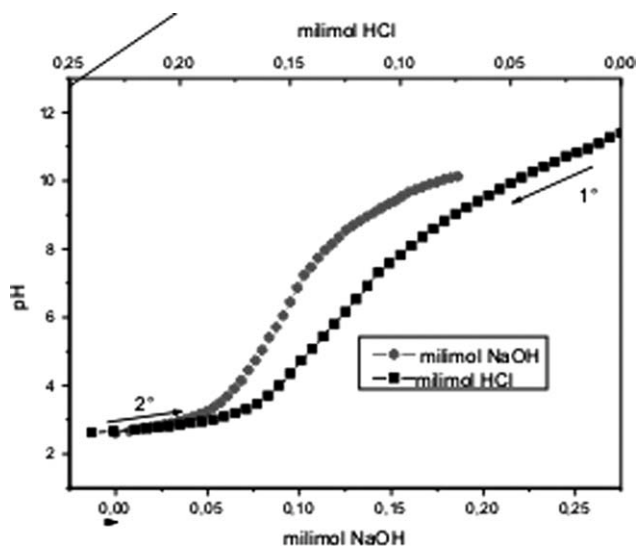

Figure 4   Titration of OATA with HCl 0.01N. The first derivate of the profile is shown (grey color).

Figure 5 Titration of OATA dissolved at pH 11.5 with HCl 0.01N (black profile) to pH 2.4 and return with NaOH 0.01N (grey profile).

may cause that pH values cannot reach as high as in the other case (curve 2).

An evidence of this proposal is that reaching the midpoint of the titration in curve 1 should require more mL of HCl than the mL of NaOH required in curve 2.

Acid–base and tautomeric equilibria

A possible explanation of its acid–base behavior is based on the fact that OATA presents in its structure several nitrogen atoms, which could protonated or deprotonated according to the pH values of the media, this fact is consistent to the results previously observed in FTIR spectra. These processes involve different equilibrium constants k_i. The possible structures of all species involved in acid–base equilibria for the tetramer and their reversible convertibility are schematically shown in Figure 6, taking into account their corresponding tautomeric forms.
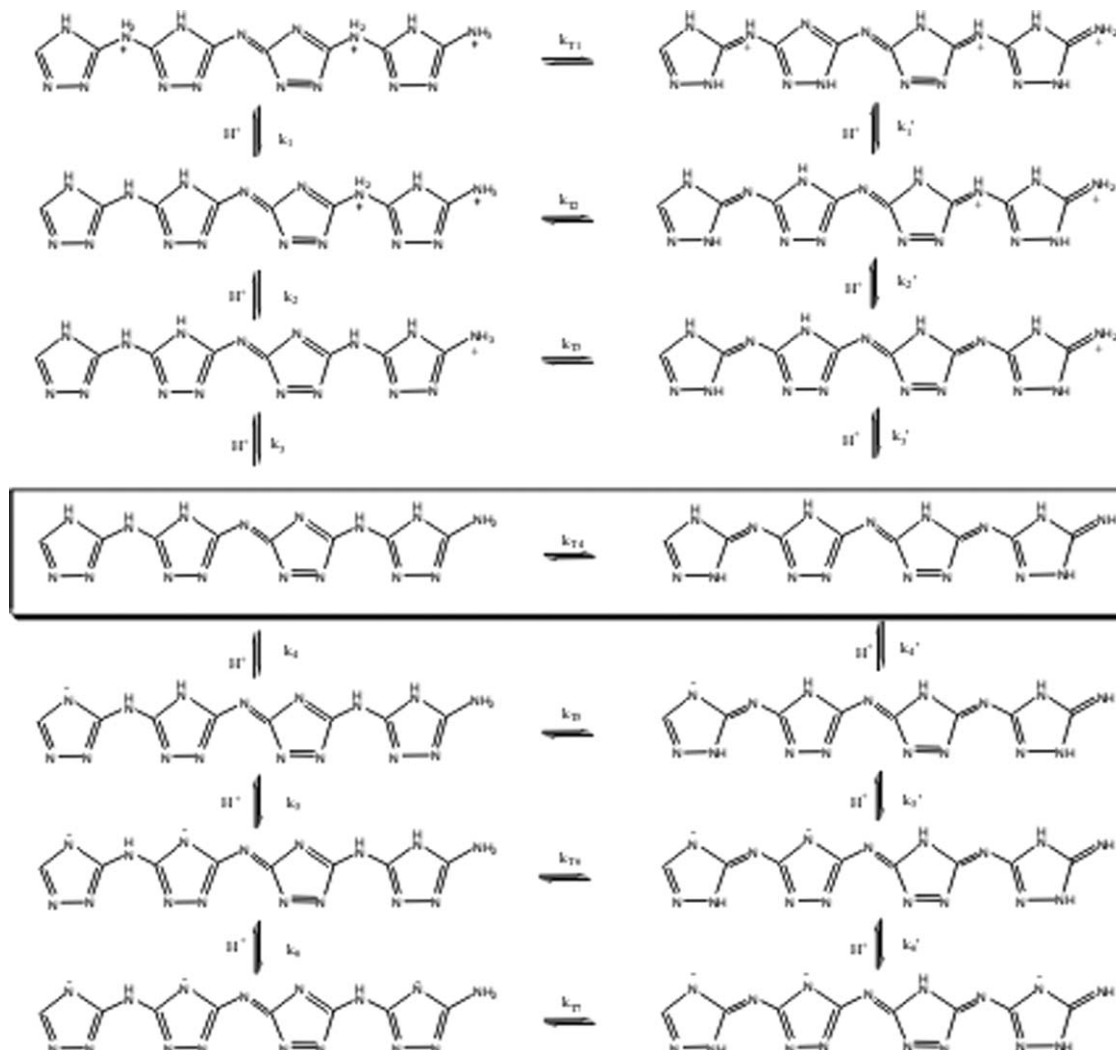
Figure 6   Acid–base and tautomeric equilibrium of OATA proposed at different pHs.
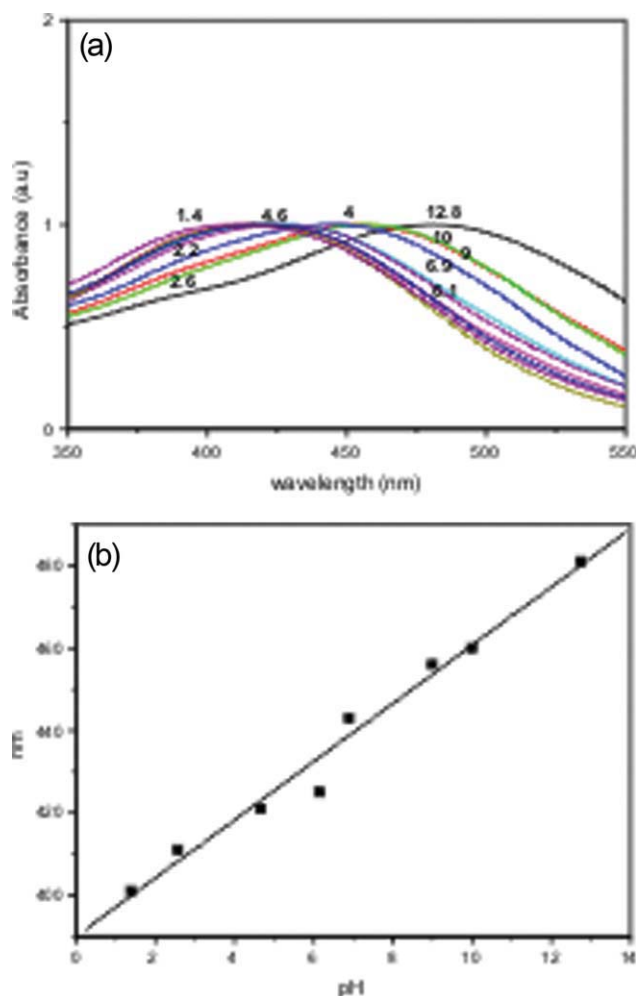
Figure 7 (a) The pH profiles (normalized) at different pH solutions. (b) Maxima spectra absorption observed for different OATA solution at different pHs. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

However, we suppose that some of them, such as k_1 and k_2, may be very closer due to the protons involved in these equilibrium seem to have similar acid–base behavior, so its order may be interchanged. The same situation can be observed to k_4 and k_5.

Color variation of OATA at different pH values

OATA solutions show a major absorption maxima at different pH values from 400 nm at pH = 1.4 to 481 nm at pH = 12.8. This absorbance corresponds to the transition $n \rightarrow \pi^*$ of imine groups; also the bathochromic shift observed, in basic medium, is related to the extension of conjugation (See Fig. 6). Color varies from light yellow in acidic conditions to burgundy in basic conditions.

In Figure 7(a), we show pH profiles obtained from the buffers solutions. It can be observed that it is not possible to identify acid equilibrium constants, prob-
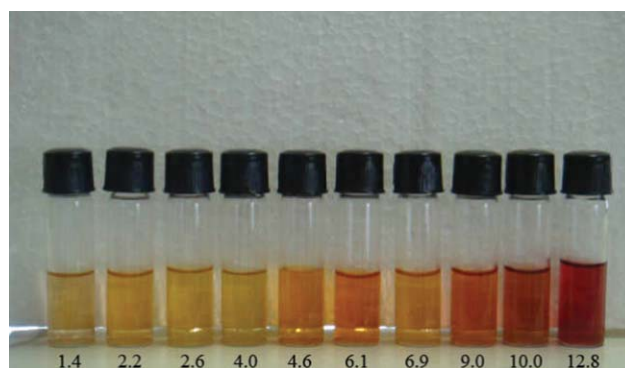
Figure 8 Color observed for OATA solutions at different pHs. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

ably as k_i values are very close together; however, in Figure 7(b), we observed that the maxima absorption is related to pH solution. Es-Safi reported a similar situation when they analyzed the spectral characteristics and color intensity, influenced by pH, of a xanthylium salt pigment.[16]

In Figure 8, we show the photographic of the OATA solutions at different pHs obtained from buffer solutions. It is possible to appreciate the color variation depending on pH solution.

The same variation is observed with OATA-embedded filter paper.

To explore a possible application of OATA as an acid–base endpoint indicator, the experiment showed in Figure 9 is proposed.

A solution of 0.01M HCl was titrated by 0.01M NaOH solution and a diluted and neutral solution of OATA as indicator was added. In acidic media, the indicator shows a yellow color and while titration proceeds, the solution turns to a reddish color. The endpoint is narrow and clear.
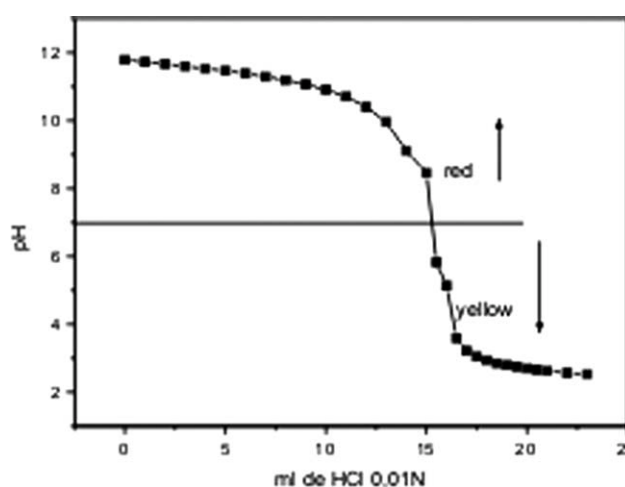
Figure 9 Titrations of HCl with NaOH using OATA neutral solution as an endpoint indicator.

OATA-embedded filter paper as vapor and solution sensor

We have used this OATA-coated paper as a sensor for ammonia solution at different concentrations (5–10–30–100–300–600 ppm). When the paper was dipped into these solutions, it turned dark red at the lowest concentration of 5 ppm in 10 min. The same paper could detect ammonia vapor from an aqueous solution having a concentration of 30 ppm. In a similar experience, Dutta et al.[9] reported that when green PANI paper was treated with ammonia solution, the paper turned blue at a concentration of 14 ppm, while it could detect ammonia vapor from an aqueous solution of 45 ppm. These results show that OATA is a very sensible oligomer for base detection.

CONCLUSIONS

This work shows that OATA evidences a complex behavior with pH, probably for the presence of several heteroatoms with characteristic response to pH. It is remarkable that OATA presents, as well as ATA (precursor), different tautomeric structures.

- The acid–base hysteresis behavior is intimately related to the mechanism of protonation and deprotonation of the different structures and the interactions relative to the solubility.
- In relatively acidic aqueous medium, the oligomer shows an intense yellow color. From pH 6.1, the color intensity increases, while there is a gradual bathochromic shift to more burgundy color. The possible use of OATA as an acid–base endpoint indicator should be considered.

- Using the OATA-containing paper, ammonia concentrations in a solution as low as 5 ppm could be measured.

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