Spectroscopy study of 5-amino-1,10-phenanthroline

ARTICLE *in* SPECTROCHIMICA ACTA PART A MOLECULAR AND BIOMOLECULAR SPECTROSCOPY · APRIL 2004

Impact Factor: 2.35 · DOI: 10.1016/S1386-1425(03)00301-9 · Source: PubMed

Available online at www.sciencedirect.com
SCIENCE DIRECT®
Spectrochimica Acta Part A 60 (2004) 781–789
SPECTROCHIMICA ACTA PART A
www.elsevier.com/locate/saa

Spectroscopy study of 5-amino-1,10-phenanthroline

Ma. Teresa Ramírez-Silva [a], Martín Gómez-Hernández [a], Ma de Lourdes Pacheco-Hernández [b], Alberto Rojas-Hernández [a], Laura Galicia [a,*]

[a] *Departamento de Química, Universidad Autónoma Metropolitana-Iztapalapa, Apartado Postal 55-534, 09340 México, D.F., Mexico*
[b] *Centro de Investigaciones Químicas, Universidad Autónoma del Estado de Hidalgo, Carr. Pachuca-Tulancingo Km. 4.5, 42076 Pachuca, Hidalgo, Mexico*

Received 6 May 2003; received in revised form 30 June 2003; accepted 1 July 2003

Abstract

Acidity constants for the 5-amino-1,10-phenanthroline (5-Aphen) were determined in aqueous media, using SQUAD and SUPERQUAD programs. Spectrophotometry and potentiometry data were fitted to the best model to enable correlation of the following acidity equilibria: 5-AphenH $=$ 5-Aphen $+$ H^+ ($-\log K = 5.78 \pm 0.03$) and 5-AphenH_2 $=$ 5-Aphen $+$ $2H^+$ ($-\log K = 6.89 \pm 0.07$). UV absorptivity coefficients obtained suggest that the first protonation takes place on the nitrogens of the heterocycle ring and the second protonation could take place on the amino group. As expected, the electrochemical evidence of the 5-Aphen species depends on the degree of protonation.

Keywords: Spectroscopic study; 5 Amino-1,10 phenanthroline; Acidity constants

1. Introduction

The study of the 1,10-phenanthroline started with the evaluation of its capacity to form metallic complexes that were used as redox indicators for oxidation–reduction titrations in quantitative analysis, when Walden et al. [1,2] described the use of the said complexes as indicators with a high redox potential. To obtain indicators able to attain different potential values, researchers such as Smith and Getz [3], and Case [4] carried out studies concerning the effect of different substituents on the 1,10-phenanthroline molecule and obtained a significant number of colorimetric indicators for use in redox titrations within the 0.87–1.33 V potential range.

A study was carried out on the effect of substituents over different positions of the 1,10-phenanthroline molecule (Fig. 1). It was found that the positions related to nuclephilic substitution were 2, 4, 7 and 9, whereas those related to electrophilic substitution were 3, 5, 6, and 8 where the electron densities were higher. Hydrogen substitution for other groups in any of these positions could cause appreciable alteration on its properties. Substitutions were carried out on position 5 with different groups such as: nitro, methyl, chloride, bromide, hydroxyl, phenyl and amine.

Several researchers have undertaken studies to elucidate the chemical properties of these molecules and on the determination of their acidity constants using different methods; namely, the acidity constants for the 1,10-phenanthroline reported by Lee et al. [5] were 4.77 at 25 °C, obtained by means of potentiometry and conductimetry determinations. In that same respect, Krumholz [6] carried out spectrophotometic determinations and obtained a value for the constant of 4.92 at 20 °C. However, later on Schilt and Smith [7] reported a constant of 4.86 while Yamasaki and Yasuda [8] reported 4.92 using potentiometry. Up to now there are about 50 publications on the determination of the acidity constants for the 1,10-phenanthroline, with the results for the said constants reported in the 4.5–5.2 range, using different methods; there were 89% using potentiometry, 7% with spectrophotometry, and the remaining used other methods.

The constants for the molecules with substitution on position 5 of the 1,10-phenanthroline have been calculated by Schilt and Smith [7], Banks and Bystroff [9], Brandt and Gullstrom [10], Yasuda et al. [11], Steinhaus and Margerum [12] and James and Williams [13]; however, the majority effected their calculations by means of potentiometry methods considering the formation of metal-complexes. For the particular case of the 5-amino, the assessment was done

* Corresponding author. Tel.: +52-55-58044670; fax: +52-55-58044666.
E-mail addresses: lgl@xanum.uam.mx, mtrs218@xanum.uam.mx (L. Galicia).

1386-1425/$ – see front matter © 2003 Elsevier B.V. All rights reserved.
doi:10.1016/S1386-1425(03)00301-9

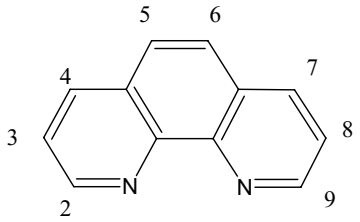

Fig. 1. Chemical structure of the 1,10-phenanthroline.

in a non-aqueous medium and from measurements of the potential during copper complex formation, using the equilibrium competence method. The latter is widely used in potentiometry and spectrophotometry using different metals that interact with the molecule of interest; the complex formation constants as well as the acidity constants of the different metal-complexes can be calculated. However, one of the problems likely to be found is that some of the properties of the organic species may not be determined or that they may become masked by the metal.

The following data in Table 1 shows a synopsis of the studies on the determination of the acidity constants of different orthophenanthrolines substituted in position 5, which in general considered the determination with the equilibrium competence method.

As can be noted from Table 1, there are only a few spectrophotometry studies (see Banks and Bystroff [9] and Steinhaus and Margerum [12]) while all the other studies were done by potentiometry methods, in aqueous and non-aqueous media. However, as mentioned before, the determination of the acidity constants was carried out by competitive methods, although for the particular case of the 5-Aphen, which is a molecule that has gained in importance, there is only one study carried out in a non-aqueous medium [13].

Table 1
Acidity constants of the 5-susbtituted 1,10 phenanthrolines

Species	pK_a	Media	Method	Reference
5-Chloro	3.43	Non-aqueous	Potentiometry	[13]
	3.33	Aqueous	Spectrophotometry	[9]
	4.26	Non-aqueous	Potentiometry	[10]
5-Bromo	4.2	Aqueous	Spectrophotometry	[9]
5-Methyl	5.26	Aqueous	Potentiometry	[11]
	5.23	Non-aqueous	Potentiometry	[10]
5-Nitro	3.57	Non-aqueous	Potentiometry	[10]
	2.8	Non-aqueous	Potentiometry	[13]
	4.18	Aqueous	Spectrophotometry	[9]
5-Phenyl	4.03	Non-aqueous	Potentiometry	[13]
	4.80	Non-aqueous	Potentiometry	[10]
	4.72	Non-aqueous	Potentiometry	[7]
5-Sulfo	5.6	Aqueous	Spectrophotometry	[12]
5-Amine	5.23	Non-aqueous	Potentiometry	[13]

The 1,10-phenanthroline and its derivate the 5-Aphen are some of the most widely used chelating ligands in coordination chemistry. The ligands or their complexes have found application in different areas such as in molecular catalysis, solar energy conversion, colorimetric analysis, herbicides, molecular recognition, self-assembly, antineoplastic agents, nucleic acid probes and the development of luminescence base sensor for pH, anions and cations [14–16]. Therefore, due to the relevance that these kinds of molecular systems (1,10-phenanthroline and its derivate) involve in the development of technological devices, it is important to gain insight their chemical features.

In particular it is important to mention that the 5-Aphen has shown the capacity to form conducting polymer films: this property has been studied in non-aqueous media [17–21], although it is a fundamental consideration to carry out the present work, that its behaviour has not been thoroughly studied in aqueous media.

In order to form conductive films of the chemical species derived from 5-Aphen, it becomes mandatory to find out what are the chemical species in a solution of the system. The process could be carried out more effectively depending on whether the monomeric species initiate the polymerization process.

The 5-Aphen has not been thoroughly studied: in acid solutions, the 5-Aphen is capable of forming different protonated species depending on the $[H^+]$/[5-Aphen] ratio that may exhibit different stoichiometries of the $[5\text{-Aphen}H_n]^{n+}$ type which have not been fully characterized yet.

Because of the interesting applications that can be developed from the knowledge of the chemical behaviour of 5-Aphen, a study related with the determination of the acid–base equilibrium constants (pK_a) is presented in this paper. Experiments were carried out in a wide pH interval ($0 < pH < 10$) to determine all the chemical equilibria in which these species are involved in aqueous solutions.

2. Experimental

2.1. Solutions

5-Aphen (Polysciences) solutions were prepared in HCl media (Merck) to determine the acid–base equilibrium constants. The range of concentrations selected was 4×10^{-3} to 5×10^{-5} M adding HCl at different concentrations. Potentiometry and spectrophotometry studies were carried out to validate the presence of the chemical species formed. An electrochemical cyclic voltammetry study was performed to confirm the effect that the suggested species could have on independent measurements.

2.2. Spectrophotometry study

5-Aphen solutions were prepared in HCl, 1.0 M media (at constant ionic strength). The pH range for the study ($0.1 <$

pH < 9.9) was adjusted by adding aqueous solutions of NaOH. Absorption spectra were obtained from these solutions, using Lambda 20 Perkin-Elmer spectrophotometer in the 200–400 nm wavelength range, with a 240 nm/min scan speed. Quartz cells with an 0.5 and 1.0 cm optic path length (l) were used. The experiments were done at $25 \pm 0.5\,^{\circ}C$, using a Cole Palmer Polystat bath.

2.3. Potentiometry study

Acid–base titrations were done for 5-Aphen/HCl solutions (1:2 ratio). Different concentrations of 5-Aphen were used (2.5×10^{-4}, 4.0×10^{-3} and 3.0×10^{-3} M) in aqueous media with chlorides using NaOH aqueous solutions (Merck, titrated and decarbonated) as titrant.

The pH was measured using two different procedures: the first used an automatic titrator TT-Processeur 2, Tacussel equipped with 20 ml automatic burette with a 0.01 ml precision. The second used a Tacussel pH-meter model LPH430T (pH±0.001) equipped with a combined glass–AgCl/Ag electrode, adding the titrant solution by means of a digital burette Brand II with a precision of 0.03 ml. The experiments were carried out at controlled temperature ($25 \pm 0.5\,^{\circ}C$) in a double walled cell and a Cole Palmer Polystat temperature controlled bath.

2.4. Electrochemistry study

Using cyclic voltammetry to assess the electrochemical behaviour, the experimental conditions selected to study the system used 5-Aphen 4×10^{-4} M solutions in chloride media with a BAS 100-B potentiostat for potential programming; all electrochemical experiments were performed at room temperature. A typical three-electrode cell was used: with a carbon paste electrode as working electrode, a saturated mercurous sulphate electrode (SME) as reference (SME = $Hg/Hg_2SO_4/K_2SO_4$) and a large area graphite bar as a counter electrode. Graphite powder 99.99% pure (Alfa Aesar) was mixed with mineral oil (Fluka) to obtain the carbon paste electrode. The pH was adjusted to (a) 1.0, (b) 4.0, (c) 10.0.

3. Results and discussion

3.1. Spectrophotometry study

3.1.1. 5-Aphen stability in aqueous solutions

In order to analyze the stability of the 5-Aphen, absorption spectra as a function of time were registered with a 5-Aphen 5×10^{-4} M solution in H_2SO_4 0.5 M (pH = 0.3), with its behaviour shown in Fig. 2. After 6 months storage,

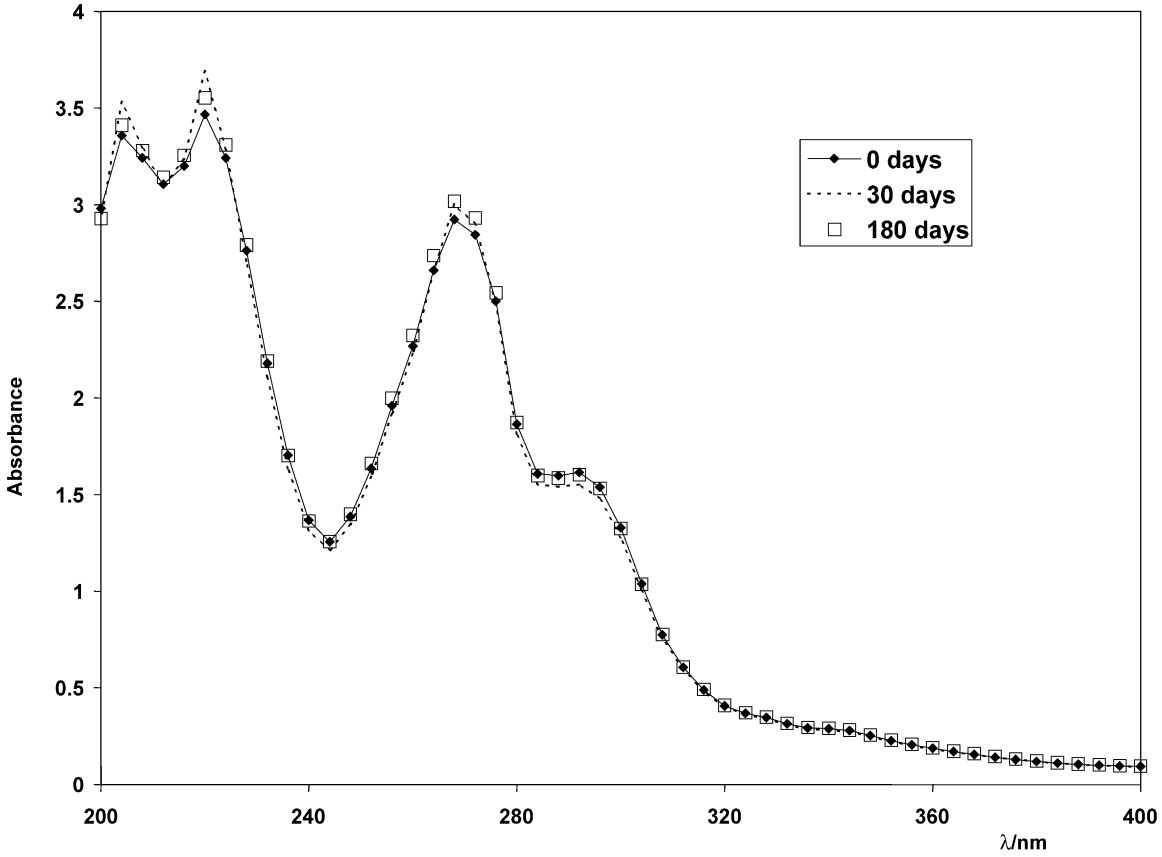

Fig. 2. Absorption spectra of the 5-Aphen 5×10^{-4} M in H_2SO_4 0.5 M (pH = 0.3) registered as a function of the time at 0, 30 and 180 days.

the absorption spectra were repeated to register the changes in absorbance at $\lambda = 268$ nm that were $\Delta A = 0.095$. Therefore, because of their magnitude they are considered negligible. The obvious conclusion from the study is that the 5-Aphen is stable during the period used for the experiments to determine the constants.

3.1.2. Species and equilibrium constants determination

A spectrophotometry study was done to collect information on the behaviour of the 5-Aphen species. A series of UV absorption spectra were registered at different pH values, using 5-Aphen solutions of different concentrations: 5×10^{-4} and 7.5×10^{-5} M. Fig. 3 shows the family of spectra obtained for both concentrations between 200 and 400 nm from pH = 0.6 to 10.0. It can be noted that the spectra show characteristic absorption bands, which appear shifted with the pH changes. For the 7.5×10^{-5} M concentration, the bands are much finer, and the wavelength maxima of the absorption peaks are much more defined. For the study of the concentrated solution, cells with a 0.5 cm path length were used so that the detector response was not saturated.

To obtain evidence as to the number of species that could be present in solution, the experimental spectra were fed into the computational program TRIANG [22], which is used to elucidate the number of species capable of interacting with the electromagnetic radiation. After an input of 50 wavelengths and 24 pH values, the results showed that there were between two and four absorbing species present in the pH interval studied. Hence, there could exist between 1 and 3 acid–base equilibria associated with the 5-Aphen.

The spectra obtained for both concentrations were fed into the computational program SQUAD [23] used to calculate the equilibrium constants. After considering different models for 1–3 acid–base equilibria, the best results obtained having the best refinement consider the existence of three acid–base species present and two chemical equilibrium equations. The results are shown in Table 2.

As can be observed in Table 2, the results obtained for both concentrations are very similar: for the 7.5×10^{-5} M concentration the statistics obtained are better (as the absorption bands are better defined).

The absorptivity coefficients calculated by SQUAD for the set of spectra with the smaller concentration are presented in Fig. 4. As it can be observed, the uncertainty on the molar absorptivity values obtained is acceptable ($\sigma \leq 10\%$). Note from Fig. 3 that the spectroscopic responses of the 5-Aphen species can be compared with previous works for *o*-phen [24].

Table 3 shows the values for the wavelength maxima and isosbestic points observed for the species present in *o*-phen (underline) and 5-Aphen (bold) systems, so that their behaviour can be compared.

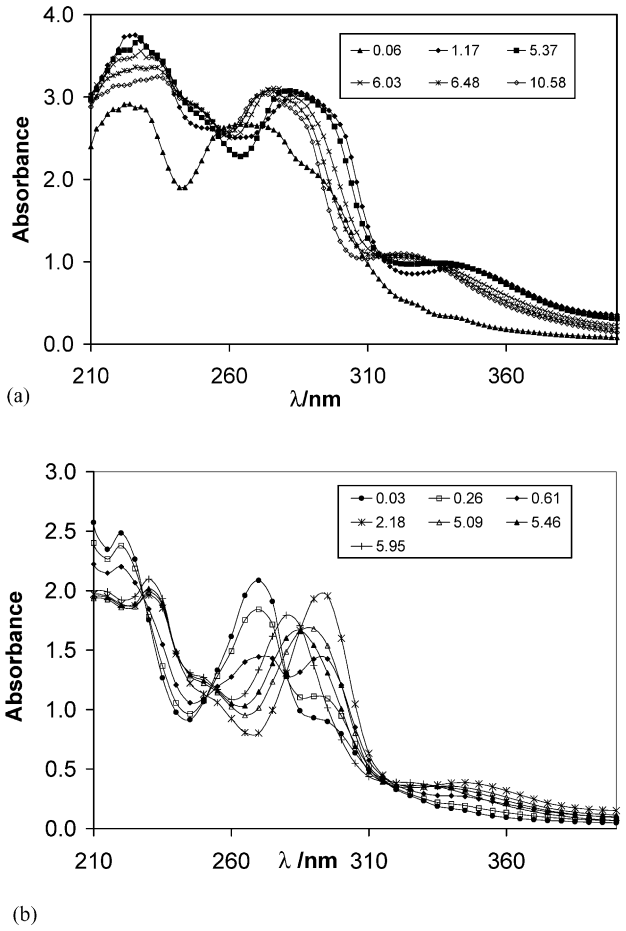

Fig. 3. Experimental spectra for the system 5-amino-1,10-phenanthroline/HCl/H_2O: (a) $[5\text{-Aphen}]_{total} = 5.000 \times 10^{-4}$ M, (b) $[5\text{-Aphen}]_{total} = 7.545 \times 10^{-5}$ M.

Table 2
Acid–base equilibria best refined with the SQUAD program for selected data from the UV-spectra set

Case	Equilibria	$[5\text{-Aphen}]_{total}$ ($\times 10^5$) (mol dm^{-3})	$\log \beta_i \pm \sigma$	σ ($\times 10^2$)	U
1	5-Aphen + H = 5-AphenH	10.0	5.78 ± 0.03	6.00	
	5-Aphen + 2H = 5-AphenH_2		6.89 ± 0.07		3.5
2	5-Aphen + H = 5-AphenH	50.00	5.70 ± 0.02	4.25	
	5-Aphen + 2H = 5-AphenH_2		6.91[a]		2.0

Twenty-five absorption spectra were used with 40 different values of wavelength.
[a] This value was constant throughout the refinement.

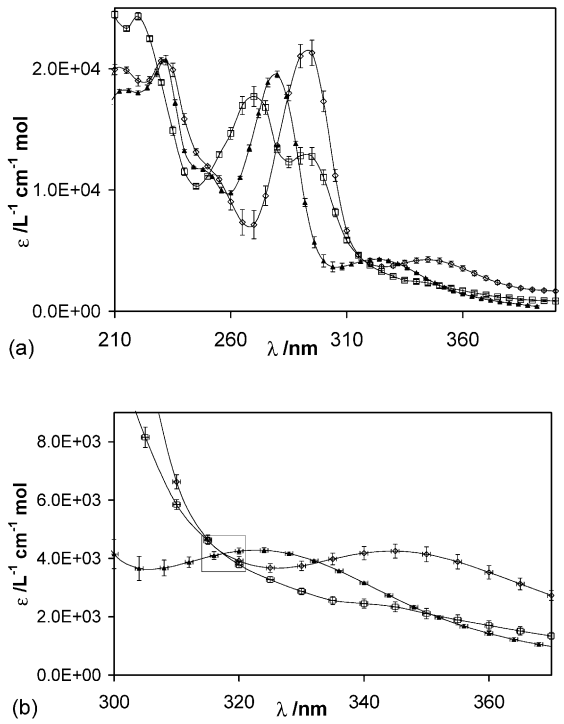

Fig. 4. Molar absorptivity coefficients for the 5-Aphen species (▲), 5-AphenH (◇) and 5-AphenH$_2$ (□): (a) values obtained with SQUAD for the wavelength interval between 200 and 400 nm, (b) zoom of (a) allows a better view the isosbestic point of the three species.

3.1.3. Spectral characteristics of the 5-amino-1,10 phenanthroline in relation with its species

Comparing the spectral behaviour for the systems of the 5-Aphen and *o*-phen, it can be observed a general bathochromic shift of the isosbestic points, while the first system shows a triple isosbestic point for a wavelength of 317.5 ± 0.4 nm. The uncertainty in the wavelength was considered from the accuracy and reproducibility specified in the Lambda 20 spectrophotometer (Perkin-Elmer).

From Table 3, we can point out that in terms of UV spectroscopy, the species *o*-phen and *o*-phenH can be considered analogous to the 5-Aphen and 5-AphenH species with a hypsochromic shift of 10–20 nm caused by the amino substituents in position 5 of the molecule. Possibly the electronic transitions in an intermediate wavelength (400 nm > λ > 250 nm) are caused by molecular orbitals in which nitrogen atoms from the heterocycle are involved.

For the bands with shorter wavelength (250 nm > λ > 200 nm), the observed shift of approximately 20 nm was bathochromic. The only transition for *o*-phen in the short wavelength region unfolds in two in the case of 5-Aphen and the change in the probability of the transition decreases considerably from *o*-phen to 5-Aphen. Maybe this is due to the electronic transitions observed at shorter wavelength that are caused by molecular orbitals from the heterocycle where their nitrogens are not involved but where the amino group can have a strong influence. This could be an indication that the first proton attaches between the nitrogen groups in the ring and not in the amino group.

Regarding the behaviour of the absorptivity coefficients for the *o*-phenH$_2$ and the 5-AphenH$_2$ species they are indeed different, because for short wavelengths (λ < 300 nm) the shift observed in the absorption bands of shorter wavelength is hypsochromic. For the *o*-phenH$_2$, the two bands at shorter wavelengths are not present for the 5-AphenH$_2$ for which there was only one band, as can be noted also from Table 3. Moreover, for the case of the *o*-phen species, the bathochromic shift of the central transition increases with the degree of protonation (*o*-phen: λ_{max} = 265 nm, *o*-phenH: λ_{max} = 270 nm, *o*-phenH$_2$: λ_{max} = 280 nm). As for the species of the 5-Aphen, the shift observed is not always of this kind (5-Aphen: λ_{max} = 280 nm, 5-AphenH: λ_{max} = 292 nm, 5-AphenH$_2$: λ_{max} = 270 nm). This could be an indication that the second protonation observed for 5-AphenH$_2$ takes place at the amino group.

Finally, the value of the estimated pK_a for the *o*-phenH$_2$ (−1.6) does not make it feasible for the value for the 5-AphenH$_2$ (1.11 ± 0.04) estimated by SQUAD, to be explained by the distant substitution of the amino group (in position 5 in the heterocycle).

3.2. Potentiometry study

Acid–base titrations were obtained using 5-Aphen aqueous solutions of (0.25–4.0) × 10^{-3} M in HCl 8 × 10^{-3} M concentration range, titrating them with NaOH 1 × 10^{-2} M. Fig. 4 shows the typical titration curve for 4.0 × 10^{-3} M in HCl 8 × 10^{-3} M.

It can be noted that there are two end points that are better defined for the higher concentration solution, which are associated to the titration of two different protons present in the system. These results agree well with the spectrophotometry study.

3.2.1. Species and determination of equilibrium constants

Data selected from the curves shown in Fig. 5 were fed into SUPERQUAD [25]: the better possible refinement obtained are presented in Table 4.

The value for log β_2 that includes the acidity constant pK_{a1} = 0.91 was not determined by means of a titration curve. This is due to very scant information available from biprotonated species (5-AphenH$_2$) in the conditions used for the potentiometric titration because they were not carried out for pH values <2.5. This is why the value for log β_2 used to feed SUPERQUAD in the case of the potentiometric study was the one obtained from the spectrophotometric data.

The results show acceptable values for log β_1 and −log K_w for potentiometric curves. As for the value for log β_1, it is practically the same as that obtained from spectrophotometric data. The best statistical refinement was considered to be the one in better agreement with the spectrophotometry study.

Table 3
Comparison of the wavelength for the maxima, molar absorptivity coefficients and isosbestic points for the species present in the systems for 1,10-phenanthroline (λ_{iso}, underline) and 5-amino-1,10-phenanthroline (λ_{iso}, bold)

Spectral features	Species					
	o-Phen	5-Aphen	*o*-PhenH	5-AphenH	*o*-PhenH$_2$	5-AphenH$_2$
λ_{max1} (nm)		215	208		205	–
	229	232 b	220	228 b	225	220 h
$\epsilon_{\lambda_{max1}}$ ($\times 10^{-4}$) (dm^3 mol^{-1} cm^{-1})		1.82 ± 0.02	2.9		2.95	
	3.80	2.06 ± 0.05	2.90	2.28 ± 0.03	2.50	2.64 ± 0.03
λ_{max23} (nm)	265	252 sh	270	252 sh	280	270 h
$\epsilon_{\lambda_{max2}}$ ($\times 10^{-4}$) (dm^3 mol^{-1} cm^{-1})	2.60	1.12 ± 0.02	2.70	1.10 ± 0.01	3.80	1.77 ± 0.08
λ_{max3} (nm)	285 sh	280 h	302	292 h	295 sh	292 h
$\epsilon_{\lambda_{max3}}$ ($\times 10^{-4}$) (dm^3 mol^{-1} cm^{-1})	0.80	1.95 ± 0.03	0.50	1.96 ± 0.02	0.70	1.30 ± 0.07
λ_{max4} (nm)					307	
		324		344	318	348 sh
$\epsilon_{\lambda_{max4}}$ ($\times 10^{-4}$) (dm^3 mol^{-1} cm^{-1})					0.80	
		0.43 ± 0.01		0.40 ± 0.04	0.60	0.22 ± 0.18
λ_{iso1} (nm)	224	**232** b			224	**232** b
	221	**261** b	221	**261** b		
			208	**228** b	208	**228** b
λ_{iso2} (nm)	275	**284** b			275	**284** b
	268	**282** b	268	**282** b		
			225		225	
λ_{iso3} (nm)	287				287	
	285	**317.5** ± **0.4** b	285	**317.5** ± **0.4** b		**317.5** ± **0.4** b
			272		272	
λ_{iso4} (nm)	294	**333** b			**294**	**333** b
	293	**336** b	293	**336** b		
			324	**351** b	324	**351** b

b, Bathochromic shift; sh, shoulder; h, hypsochromic shift.

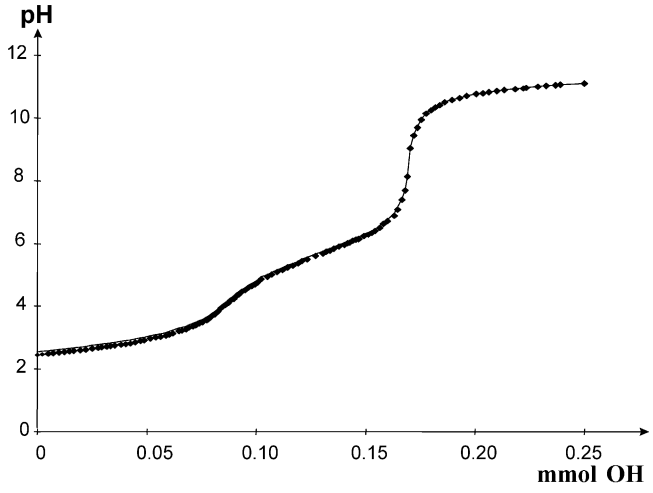

Fig. 5. Typical titration curve for the 5-amino-1,10-phenantroline/HCl/H_2O system with NaOH. The initial proportion of the mixture 5-Aphen: HCl was 1:2; 20 ml of 5-Aphen 4.0×10^{-3} M in HCl 8×10^{-3} M.

The values of the acidity constants obtained can be ascribed to the amino group $pK_{a1} = 1.11$ and the imine group $pK_{a2} = 5.78$, which can be verified using the ACD/pK_a^* program [26] that calculates theoretically the acidity constants for this molecule: the value $pK_{a1} = 2.29 \pm 0.30$ was ascribed to amino group whereas the theoretical value for the acidity constants for this molecule of $pK_{a2} = 5.80 \pm 0.30$ was for the imine group. The agreement found with the program was very good with respect to the pK_{a2}, and was different with respect to first pK_{a1}, however, it gives support to the idea that there exists two pK_a associated to this molecule and that the assignation of the acidity of the amino and imine groups is correct.

3.2.2. Species distribution diagram

After obtaining the constants for the formation equilibria of the 5-Aphen species, it was possible to establish the acid–base equilibria for the systems:

5-AphenH = 5-Aphen + H^+	$pK_{a1} = 1.11 \pm 0.04$
5-AphenH$_2$ = 5-Aphen + 2H^+	$pK_{a2} = 5.78 \pm 0.03$

Moreover, from the constant values obtained by the best refinements using the programs for analyzing the poten-

Table 4
Acid–base equilibria processed with SUPERQUAD, for selected data of the titration curves showed in Fig. 4 with the best possible refinement

Titration	Equilibria	$[5\text{-Aphen}]_{Total}$ ($\times 10^4$) (mol dm^{-3})	$\log \beta_i \pm \sigma$ or $-\log K_w \pm \sigma$	Number of points	U ($\times 10^4$) (σ (mV)) [χ^2]
1	(1) 5-Aphen + H = 5-AphenH	40.2	5.448 ± 0.057	150	2.387
	(2) 5-Aphen + 2H = 5-AphenH$_2$		6.630[a]		(12.8)
	(3) H_2O = H + OH		13.650[a]		29.42
2	(1) 5-Aphen + H = 5-AphenH	20.4	5.906 ± 0.080	135	0.728
	(2) 5-Aphen + 2H = 5-AphenH$_2$		6.630[a]		(7.4)
	(3) H_2O = H + OH		13.936 ± 0.012		47.22
3	(1) 5-Aphen + H = 5-AphenH	3.95	5.676 ± 0.030	65	0.017
	(2) 5-Aphen + 2H = 5-AphenH$_2$		6.890[a]		(1.7)
	(3) H_2O = H + OH		13.652 ± 0.008		6.48

The pH interval studied was from the initial mixture [HCl/[5-Aphen] = 2/1 until NaOH was added in excess (final pH 11.0).
[a] This value was kept constant throughout the refinement.

tiometric and spectrophotometric curves, a distribution diagram for the chemical species was constructed, as shown in Fig. 6. The pH intervals for which certain species of the system 5-amino-1,10-phenanthroline are predominant can be observed. The diprotic species (5-AphenH$_2$) predominates in the pH < 0.91 range, while the monoprotic species (5-AphenH) predominates in the 0.91 < pH < 5.71 range: the neutral species (5-Aphen) predominates when pH > 5.71.

3.3. Electrochemical behaviour of the 5-Aphen systems in aqueous solution

From the chemical speciation results presented, studies were performed in order to verify the 5-AphenH$_2$, 5-AphenH and 5-Aphen formation under the experimental conditions predicted in this study.

Based on the theoretical–experimental information for chemical speciation obtained, three experimental conditions were selected for analyzing the electrochemical behaviour of each of the predicted species. Electrolytic solutions were prepared using a 0.1 M chloride solution, to which a 2×10^{-3} M 5-Aphen solution was added, at three different pH values.

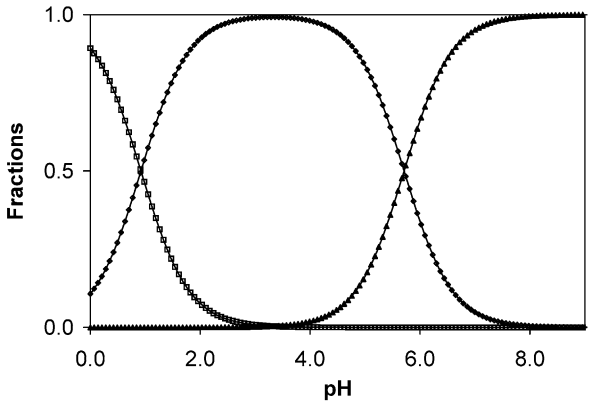

Fig. 6. Distribution diagram for the species of the 5-amino-1,10-phenantroline system in aqueous solutions as a function of pH: 5-Aphen (▲), 5-AphenH (◇), 5-AphenH$_2$ (□).

Fig. 7 shows the voltammograms for 5-Aphen at (a) pH = 1.0, (b) pH = 4, (c) pH = 10, potential range +0.8 to −0.8 V/SME with the scan starting at the null current potential towards anodic values and then reversed.

It was found that the oxidation takes place in two stages. The potential values at which the process occurs are reported in Table 5.

The oxidation process for 5-Aphen depended strongly on pH. The oxidation potential increased with the protonation degree of the 5-AphenH$_2$ that will be oxidized at more anodic potentials than the 5-AphenH and 5-Aphen. The reduction process of the species generated during the oxidation process was found to depend also on the experimental conditions.

The voltammogram in Fig. 7a indicated that the reduction process was strongly influenced by adsorption of species onto the electrode (peak III); when the potential scan was reversed, an oxidation process of the species adsorbed on the electrode was observed (peak IV).

The reduction processes for both cases, see the voltammograms in Fig. 7b and c, appeared at more cathodic potentials. It is interesting to point out that as the pH of the solution increased, the species involved in the process are not as easily reduced.

The voltammogram in Fig. 7b shows a reduction process (peak III) and its corresponding oxidation process (peak IV). This redox process is being controlled by diffusion of the species to the electrode. The voltamogram in Fig. 7c presents a totally irreversible reduction process which is carried out in

Table 5
Potential values corresponding to the first and second oxidation peaks for 5-Aphen in chloride media 0.1 M

pH	Species	E_I (mV)[a]	E_{II} (mV)[a]
1.0	5-AphenH$_2$	488	704
4.0	5-AphenH	400	580
10.0	5-Aphen	235	572

[a] Potentials referred to SME.

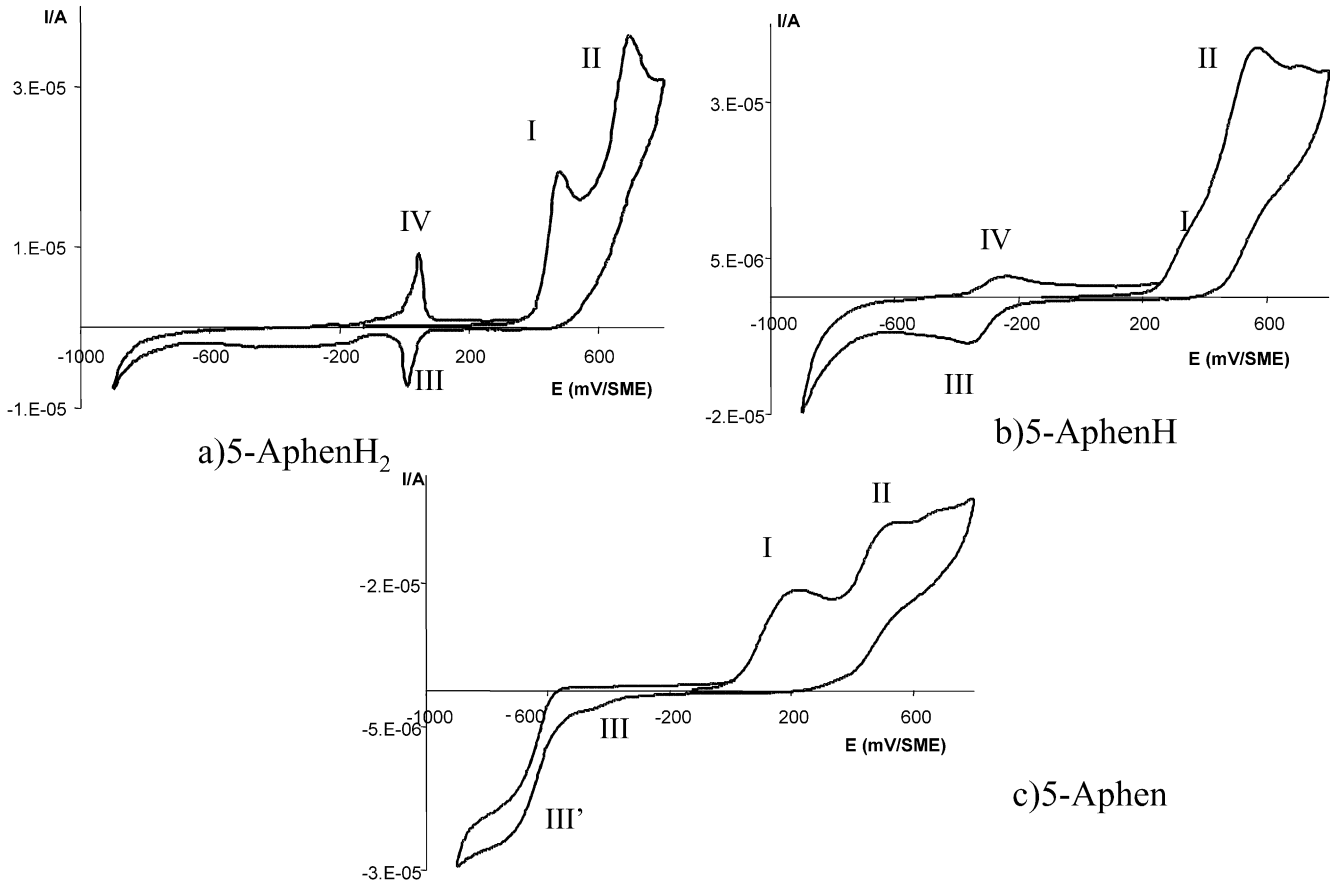

Fig. 7. Voltammetric behaviour of the 5-Aphen 2×10^{-3} M in a 0.1 M chloride solution at different pH values: (a) pH = 1.0, (b) pH = 4.0 and (c) pH = 10.0. The potentials are referred to the saturated mercurous sulphate electrode (SME).

two stages (III, III′); when the potential scan is reversed, the oxidation response of the reduced species was not observed.

As it can be observed, the electrochemical behaviour of the 5-Aphen species is affected by the degree of protonation of the molecules, and in turn, this depended on the pH of the solution. The protonation/deprotonation reactions coupled to the redox processes determined the electrochemical behaviour of the 5-Aphen system and the adsorption properties of the species. The voltammograms in Fig. 7 show that the 5-Aphen species have redox properties that allowed chemical differentiation among them, which evidence the existence of 5-AphenH_2, 5-AphenH and 5-Aphen experimentally.

4. Conclusions

The first protonation constant was determined by potentiometry and spectrophotometry, with the $\log \beta_1 = 5.71 \pm 0.06$ value having a good agreement for both techniques. The second protonation constant was determined by spectrophotometry, obtaining a value of $\log \beta_2 = 6.63 \pm 0.18$. The existence of two values for the acidity constants was confirmed for the molecule by means of the program pK_a from ACD.

By comparing the UV spectroscopy of the 5-Aphen system with the UV spectroscopy of the *o*-phen system, it is suggested that the first protonation could take place between the nitrogens of the heterocycle ring. The second protonation could take place in the amino group.

From the voltammetry studies it can be said that the redox behaviour of the 5-Aphen depended upon the protonation degree of the chemical species in solution: also it became evident that it was more difficult to oxidize the 5-Aphen species in solution with a higher protonation degree, and that the anodic oxidation of 5-Aphen is an irreversible process. Another electrochemical characteristic of 5-Aphen is the dependence of its adsorption properties on the pH of the solution, which has a fundamental influence upon the protonation/deprotonation process of the species. The experimental evidence indicated that at very low pH the species produced by the oxidation are quite easily adsorbed on the carbon paste electrode.

Acknowledgements

This work was financially supported by the CONACYT project no. 400200-5-32576-E. The authors wish to express their acknowledgement to Dr. A. Vacca and Dr. P. Gans for

the program SUPERQUAD. The authors wish to thank Dr. Romero-Romo for the English translation.

References

[1] G.H. Walden Jr., L.P. Hammett, R.P. Chapman, J. Am. Chem. Soc. 53 (1931) 3908.
[2] G.H. Walden Jr., L.P. Hammett, R.P. Chapman, J. Am. Chem. Soc. 55 (1933) 2649.
[3] G.F. Smith, C.A. Getz, Chem. Rev. 16 (1935) 113.
[4] F.H. Case, J. Am. Chem. Soc. 70 (1948) 3994.
[5] T.S. Lee, I.M. Kolthoff, D.L. Leussing, J. Am. Chem. Soc. 70 (1948) 2348.
[6] P. Krumholz, J. Am. Chem. Soc. 73 (1951) 3487.
[7] A.A. Schilt, G.F. Smith, J. Phys. Chem. 60 (1956) 1546.
[8] K. Yamasaki, M. Yasuda, J. Am. Chem. Soc. 78 (1956) 1324.
[9] C.V. Banks, R.I. Bystroff, J. Am. Chem. Soc. 81 (1959) 6153.
[10] W.W. Brandt, D.K. Gullstrom, J. Am. Chem. Soc. 74 (1952) 3532.
[11] M. Yasuda, K. Sone, K. Yamasaki, J. Phys. Chem. 60 (1956) 1667.
[12] R.K. Steinhaus, D.W. Margerum, J. Am. Chem. Soc. 88 (1966) 441.
[13] B.R. James, R.J.P. Williams, J. Chem. Soc. (1961), 2007.
[14] Y. Shen, B.P. Sullivan, Inorg. Chem. 34 (1995) 6235.
[15] Z. Murtaza, P. Herman, J.R. Lakowicz, Biophys. Chem. 80 (1999) 143.
[16] D. Roberto, R. Ugo, F. Tessore, E. Luceti, et al., Organometallics 21 (2002) 161.
[17] F.W.N. Nyasulu, H. Mottola, J. Electroanal. Chem. 239 (1988) 175.
[18] X. Ren, P.G. Pickup, J. Electroanal. Chem. 365 (1994) 289.
[19] C.D. Ellis, L.D. Margerum, R.W. Murray, T.J. Meyer, Inorg. Chem. 22 (1983) 1283.
[20] I. De Gregori, F. Bedioui, J. Devynck, J. Electroanal. Chem. 238 (1987) 197.
[21] L.G. Bachas, L. Cullen, et al., J. Chem. Soc., Dalton Trans. 9 (1997) 1571.
[22] F.R. Hartley, C. Burgess, R.M. Alcock, Solution Equilibria, Wiley, New York, 1980, p. 41.
[23] D.J. Legget, Computacional Methods for the Determination of Constants, Plenum Press, New York, 1985, p. 159.
[24] R.H. Linell, A. Kaczmarczyk, J. Phys. Chem. 65 (1961) 1196.
[25] P. Gans, A. Sabatini, A. Vaca, J. Chem. Soc., Dalton Trans. (1985) 1195.
[26] ACD/pK_a of Advanced Chemistry Development Version 5.01.