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Article

The Spectrophotometric Determination of the pK_a of Pyrrolidinedithiocarbamic and Piperidinedithiocarbamic Acids, Based on Diode Array Measurements

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Neste trabalho apresenta-se um método espectrofotométrico, baseado em equipamentos com arranjo linear de diodos ("diode array"), para determinação de pK_a dos ácidos ditiocarbâmicos derivados da pirrolidina (HPyr-I) e da piperidina (HPip-II). A elevada velocidade de leitura do equipamento, torna possível minimizar o problema da decomposição dos ditiocarbamatos, em meio ácido. Os valores de pK_a obtidos foram 3.10(I) e 3.51(II), em I = 0.50 mol L^{-1} ($NaClO_4$) à 25.0 °C, sendo consistentes com os mecanismos de decomposição ácida. Apresenta-se também uma discussão baseada na forma dos espectros obtidos em meio ácido e básico e sua relação com a ordem dos valores de pK_a, a qual é inversa em relação a valores determinados anteriormente.

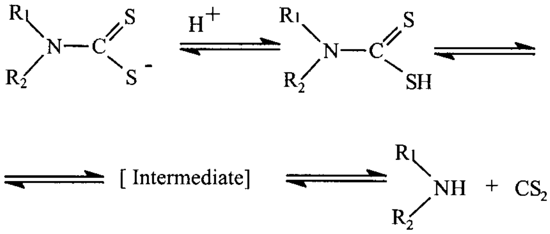
A spectrophotometric method, based on the use of a diode array spectrophotometer, is proposed in order to determine the pK_a of pyrrolidinedithiocarbamic (HPyr-I) and piperidinodithiocarbamic (HPip-II) acids. The high speed of data acquisition of the equipment made it possible to minimize the problem of acid decomposition. The values obtained were 3.10(I) and 3.51(II) in I = 0.50 mol L^{-1} ($NaClO_4$) at 25.0 °C, and are consistent with the acid decomposition mechanism. A discussion is presented based on the shape of the compound spectra in acidic and basic media and their relation to the order of the pK_a values for I and II.

Keywords: *piperidinedithiocarbamic acid, pyrrolidinedithiocarbamic acid, pK_a determination*

Introduction

Dithiocarbamates (DTC) have been widely applied in several industries (*e.g.* rubber), agriculture, medicine, organic synthesis, and in analytical chemistry (especially inorganic species analysis)[1-10]. The low stability of the DTC in acidic media has been indicated as the major limitation to the use of these versatile compounds.

Zahradnick and Zuman[11] first studied the decomposition reaction, and Chakrabarti *et al.*[12-16] proposed a degradation mechanism which may be related to the acidic form, represented by an unstable intermediate and generating an amine and carbon disulfide, according to the reaction:



(1)

These authors proposed that the instability of the intermediate, whose structure is presented in the Fig. 1, is due to the positive charge density in the carbon and nitrogen atoms of the carbamate bond (N-C), which induces the molecule decomposition in acidic media.

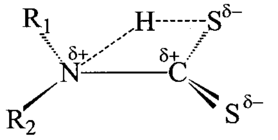


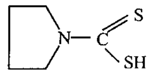
Figure 1. The acid decomposition intermediate, according to Joris *et*

Thus, the pK_a value for the DTC is an important feature since it is related to the compound stability and varies with the aminic substituent.

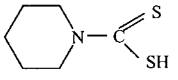
The kinetic, polarographic, or mathematical methods proposed for the pK_a measurements[12-16] are time consuming. Conventional potentiometric and spectrophotometric methods are not applicable because of the rapid decomposition that occurs in acidic media.

The present work describes the application of a relatively easier spectrophotometric method based on Volgel's proposal[17], but employing a diode-array spectrophotometer, whose reading speed permits data acquisition in such a short time that it by-passes the problem of compound decomposition. The method is applied to the pK_a value determination of pyrrolidinedithiocarbamic (HPyr) and piperidinedithiocarbamic (HPip) acids.

The structural formula of the acids are:



I-HPyr



II-HPip

Materials and Methods

All of the reagents used were of analytical grade.

DTC synthesis and characterization

The Pyr and Pip sodic salts were obtained by the reaction between the carbon disulfide and the respective amine (pyrrolidine or piperidine), in the presence of sodium hydroxide[18] in an ethanol/water 1:1 (v/v) reaction media. The white salt obtained was washed with cold ethanol and then recrystallized by dissolving in water, followed by the addition of ethanol. The solution was frozen and the white needle crystals which formed were characterized by vibrational spectrometry (ligands), atomic absorption (sodium), and thermogravimetric analysis.

Buffer solutions

The McIlvaine buffer solutions with ionic strength adjusted to 0.50 mol L^{-1} ($NaClO_4$) were prepared according to Elving *et al.*[19]. The pH of these buffers was measured with a glass electrode calibrated with conditional buffers.

These conditional buffers were solutions with an ionic strength of 0.50 mol L^{-1} ($NaClO_4$), and hydrogen ion concentrations of 1.00×10^{-2} and 1.00×10^{-4} mol L^{-1} ($HClO_4$), corresponding to pH 2.00 and 4.00, respectively[20].

Equipment

A diode-array Hewlett-Packard HP 8451A spectrophotometer and quartz cells 1.00 cm in length were used in the spectrophotometric measurements.

The ligands were characterized in a Nicolet 5SXC FTIR spectrophotometer equipped with a TGS detector in the 4.000-400 cm^{-1} range. The spectra were obtained from KBr pellets.

The number of hydration water molecules was determined in a DuPont TGA-951 thermogravimetric module, coupled with a DuPont 9900 thermal analyzer system.

The atomic absorption experiments were performed in an Intralab AA12/1475 spectrophotometer.

Procedures

All of the spectrophotometric measurements were carried out at 25.0 ± 0.1°C, using the buffer solutions previously thermostated at this temperature as blanks.

The stock NaDTC solutions (50.0 mL), at a 5.0×10^{-4} mol L^{-1} concentration, were used for the preparation of the working solutions, with concentrations ranging from 8.33×10^{-6} to 6.67×10^{-5} mol L^{-1} at pH 2.05 to 4.47. A 3.33 mol L^{-1} solution of each DTC was used in the determination of the maximum wavelength absorption of the acidic and basic forms, at pH 0.98 and 7.82, respectively.

In order to minimize the decomposition of the compounds, the solutions were prepared directly in the quartz cells. Thus 0.20 mL of the stock solution of NaDTC was transferred with an automatic pipette and introduced into 2.80 mL of the previously thermostated buffer. The mean time spent in the procedure and the reading was about 5 s, since the equipment reads the spectral range in 0.1 s.

Results and Discussion

The NaDTC characterization

In Table 1 the principal bands found in the vibrational spectroscopy measurements are presented, compared with the literature values for the groups C=S, $N-CS_2$, and C-N for the compounds NaPyr and NaPip.

The atomic absorption experiments evidenced the presence of 10.80% Na in the $NaPyr.2H_20$ (calculated = 11.20%) and 9.94% (m/m) in the $NaPip.2H_20$ (calculated = 10.49%). The thermogravimetric results confirmed the presence of two hydration water molecules for both com-

Table 1. The principal IR bands observed, compared with the literature values.

Compound	C=S	$N-CS_2$	C-N
$NaPyr.2H_2O$	$1005^{(1003a)}$	$1110^{(1110a)}$	$1470^{(1460a)}$
$NaPip.2H_2O$	$998^{(1003b)}$	1169	$1462^{(1455b)}$

pounds. This is consistent with the work of Kudela *et al.*[21] and Siddiqi *et al.*[22].

Molar absorptivity (ε) determination

The molar absorptivity was obtained from angular coefficients of the absorbance *vs.* concentration (mol L^{-1}) curves for the acidic and basic forms of each DTC, in the maximum wavelength (λ_{max}) region. The spectra of these compounds are presented in Fig. 2a (Pyr) and 2b (Pip), at different pH values for the acidic and basic forms. According to the literature[23], the presence of a single maximum in acidic media is due to protonation, which reduces the resonance in the N-CS_2 group.

In Fig. 3 the Lambert-Beer curves for Pyr (3a) and Pip (3b) are presented at different pH at λ_{max} for the acidic and basic forms of each compound. Table 2 presents the final results.

The values showed good agreement with those found by Shankaranarayana and Patel[23], being on the order of 10^4. The results indicate that acidic forms have smaller absorptivities than basic forms.

pK_a calculations

Substitution of the ε values in the Eqs. 2 and 3

$$A_A = \varepsilon_{A,RSH}(RSH) + \varepsilon_{A,RS^-}(RS^-) \qquad (2)$$

$$A_B = \varepsilon_{B,RSH}(RSH) + \varepsilon_{B,RS^-}(RS^-) \qquad (3)$$

which consider that the absorbance is due only to the presence of the free and protonated species at each wavelength, made it possible to calculate the concentration of acidic and basic forms in equilibrium. In the above equations, A_A is the absorbance at wavelength A, $\varepsilon_{A,RSH}$ is the molar absorptivity for the protonated form at wavelength A, ε_{A,RS^-} is the molar absorptivity for the free form at wavelength A, and **(RSH)** and **(RS^-)** are the activities of the protonated and free forms, respectively.

Table 2. Molar absorptivities, ε, determined for each DTC to both acidic and basic forms.

Compound	pH	λ /nm	ε/L mol^{-1} cm^{-1}	log ε
HPyr	0.89	272	$1.19.10^4$	4.1
Pyr^-	7.82	256	$1.45.10^4$	4.2
HPip	0.89	276	$5.26.10^3$	3.7
Pip^-	7.82	264	$1.45.10^4$	4.2

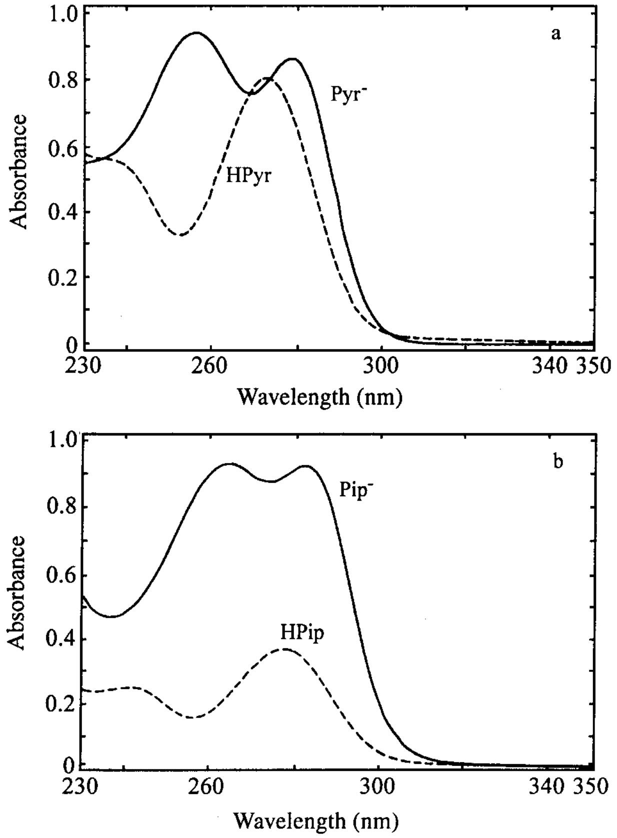


Figure 2. The Pyr(2a) and Pip(2b) spectra in acid (pH = 0.98) and basic (pH = 7.82) media.

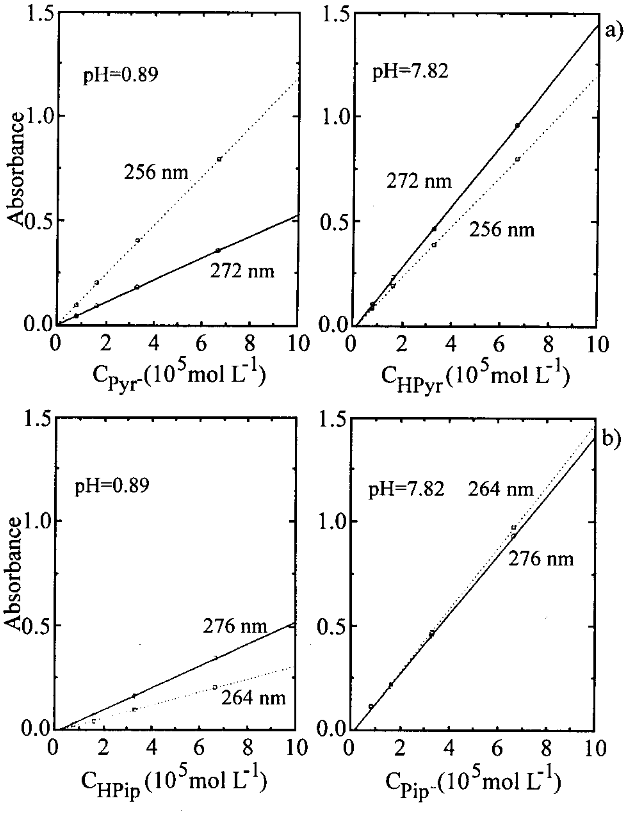


Figure 3. The Lambert-Beer law verification, in the λ_{max} of the acid and basic forms of each DTC (3a - Pyr and 3b - Pip). The angular coefficients of these curves gave the $\varepsilon_{A,RSH}$ $\varepsilon_{B,RSH}$ ε_{A,RS^-}, and ε_{B,RS^-} values.

Using the ratio of these concentrations it is possible to calculate the pK_a according the Handerson-Hasselbach equation:

$$pK = pH - \log\frac{(RS^-)}{(RSH)} \tag{4}$$

A simple computer program in the Quick Basic language (©Microsoft Co.) was developed to perform the calculations, giving the results presented in Table 3, in I = 0.50 mol L^{-1} (adjusted with $NaClO_4$) and at 25.0 °C. This program utilizes the concentrations of acidic and basic forms given by Eqs. 5 and 6, derived from Eqs. 2 and 3 system:

$$(RSH) = \frac{(A_A\,\varepsilon_{B,RS-}) - (A_B\,\varepsilon_{A,RS-})}{(\varepsilon_{A,RSH}\,\varepsilon_{B,RS-}) - (\varepsilon_{A,RS-}\;\varepsilon_{B,RSH})} \tag{5}$$

$$(RS^-) = \frac{A_B - (\varepsilon_{B,RSH}\;(RSH))}{\varepsilon_{B,RS-}} \tag{6}$$

Table 3. pK_a values determined by the spectrophotometric method, using Eqs. 5 and 6.

pH	Absorbance		L/HL	pK_a
Pyr	λ = 256 nm	λ = 272 nm		
2.05	0.7893	1.567	0.07574	3.17
2.49	0.8980	1.568	0.1922	3.21
2.66	1.086	1.633	0.3948	3.06
3.06	1.313	1.606	0.9422	3.08
3.61	1.672	1.607	3.593	3.05
4.47	1.872	1.588	30.16	2.99
			mean	3.10 ± 0.07
Pip	λ = 264 nm	λ = 276 nm		
2.05	0.5852	0.9247	0.03015	3.57
2.49	0.6674	0.9773	0.08700	3.55
2.66	0.5102	0.6920	0.1699	3.43
3.06	0.9604	1.191	0.3305	3.54
3.61	1.413	1.490	1.402	3.46
			mean	3.51 ± 0.08

Constants:

$\varepsilon_{Pyr,256}=1.45$ $\varepsilon_{Pip,264}=1.45$
$\varepsilon_{HPyr,256}=0.537$ $\varepsilon_{HPip,264}=0.316$
$\varepsilon_{Pyr,272}=1.21$ $\varepsilon_{Pip,276}=1.39$
$\varepsilon_{HPyr,272}=1.19$ $\varepsilon_{Hpip,276}=0.526$

Table 4. Summary of pK_a values from the literature and the present work.

pK_a		Conditions		Reference
Pyr	Pip	I	Temp.(°C)	
2.95	-	0.01	25.0	11
3.30	3.21	0.01	25.0	14
3.27	3.18	0.05	25.0	15
3.30	3.21	0	25.0	24
3.10	3.51	0.50	25.0	this work

The literature values and the conditions under which they were obtained are presented in the Table 4. This table shows that the values are not in agreement for HPip, possibly due to compound decomposition. Also, the order pK_{Pyr} pK_{Pip} is inverted in relation to the present results, which are consistent with the proposal of the acid decomposition intermediate, since according to the present pK_a results the Pyr is protonated at a pH more acid than the Pip, having a lower pK_a value.

It is widely known that Pyr is much more stable in acidic media than Pip[3,8,9,10], and is frequently applied in several methods of analysis in acidic conditions. The solvatation of acidic intermediates[12] is not sufficient to explain this difference, since the ligands have similar structures. For instance, $\tau_{(Pyr)}$ = 85.6 min in pH = 3.60 and $\tau_{(Pip)}$ = 3.78 min in pH = 4.85[25]. Other kinetic data are presented in Table 5, which are in agreement with the results from Vandebeek *et al.*[14]. According to these authors, the apparent rate constant (k_{ap}) and the half-life time (τ_{ap}) varies with the pH up to a certain value, at which they became constant (k_{lim} and τ_{lim}, respectively).

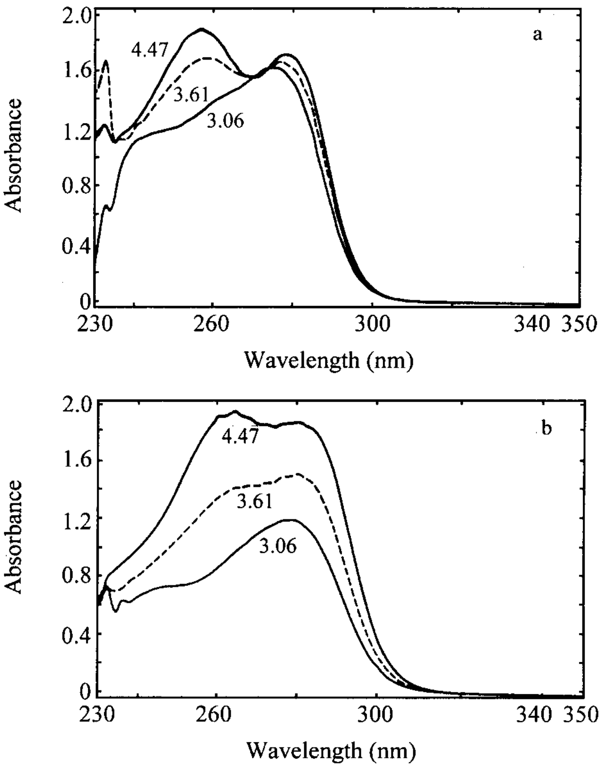


Figure 4. Variation in the spectral shape at pH 3.06, 3.61, and 4.47 for the compounds (4a Pyr and 4b Pip).

Table 5. Kinetic decomposition parameters for Pyr and Pip, at different pHs, and ionic strength adjusted to 0.50 mol L^{-1} ($NaClO_4$).

pH	$k_{ap}/10^{-4}$ min^{-1}	τ_{ap}/min	$k_{lim}/10^{-2}$ min^{-1}	τ_{lim}/min
Pyr				
3.60	81	85.570	3.1	30
4.59	9.2	753.40	2.7	27
5.80	0.65	10,664	3.0	23
		mean:	2.9 ± 0.2	27 ± 3
Pip				
4.85	1832	3.78	4.2	0.17
5.50	475	14.6	4.7	0.15
6.40	42.5	163	3.8	0.21
7.94	1.73	4,001	4.8	0.14
		mean:	4.4 ± 0.4	0.17 ± 0.03

A second point in favor of the present results is the spectral shape of the compounds at different pHs, presented in Figs. 4a and 4b for Pyr and Pip, respectively. From these curves it is possible to note that for the Pyr case at pH 3.06, a single peak appears at 247 nm (acidic form), and that two peaks are present at pH 3.61 and 4.47 at 258 and 276 nm (basic form). Thus, a spectral change corresponding to an alteration in the predominance of the forms occurred between pH 3.06 and 3.61.

In the Pip case, this spectral change appears clearly only at pH 4.47. At pH 3.06 there is only one peak at 280 nm (acid form), while at 3.61 there are two peaks, without definition, suggesting that the spectral change occurs near, but before pH 3.61.

Based on these comments it is possible to conclude that the present values are more coherent with the acid decomposition theory and the spectral change than the earlier proposed values. This has been attributed to the use of the diode array spectrophotometer, with high reading speed, technology which was not available when previous research was developed.

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