

UV STUDY OF INDOLE AND 3-ACETYLINDOLE IN PHOSPHORIC AND HYDROCHLORIC ACID SOLUTIONS

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Abstract

Protonation of indole and 3-acetylintole in phosphoric and hydrochloric acid solutions was studied by UV spectroscopy. We present pK_a values obtained by the CVA (Characteristic Vector Analysis) method. From the data, pK_a values for protonation were obtained by using the Hammett's equation: $pK_a = H_0 + \log[c(\text{BH}^+)/c(\text{B})]$. The dissociation constants and solvent parameter m^* were obtained by application of the Excess Acidity Method. The position of protonation is discussed.

Key words: UV spectra, indole, 3-acetylintole, protonation, dissociation constants, Hammett Acidity Function Method, Excess Acidity Method, Characteristic Vector Analysis.

Introduction

2,3-Benzopyrrole (indole) and 3-methylindole (skatole) are formed by decomposition of the L-tryptophan.¹ It was suggested that indole (I) and skatole are formed in the presence of enzymes. In this case I is transformed in indolyl-3-sulfuric acid and indolyl-3-glucuronic acid.¹ Some indole derivatives are plant hormones.²⁻⁶ For spectrophotometric determination of which property I and/or its derivatives, examination of the stability of the indoles in various acidic media is used as test for method validation.⁷⁻¹⁰ The results obtained from UV study of the protonation of I, indolyl-3-acetic acid, indolyl-3-propionic acid and indolyl-3-butyric acid in perchloric acid solutions¹¹ and sulfuric acid solutions,¹³ 3-methylindole, D-tryptophan, 3-acetylintole and indole-2-carboxylic acid in perchloric acid solutions¹² and sulfuric acid solutions¹⁴ are reported.

From the dissociation constants of the nine indole derivatives, values of acidity function (H_i) have been determined for sulfuric and perchloric acid in the concentration range from 0.1 to 12.0 mol dm⁻³, and from 0.1 to 6.0 mol dm⁻³ respectively,¹⁵ by means of the relation $H_i = pK_{BH^+} - \log I$. The dissociation constants (pK_a values) of the other indole derivatives are determined using H_i values.¹⁶⁻²² By application of the Excess Acidity Method,²³ pK_a values for I and 1-methylindole are determined.²⁴

In the present, we studied the influence of solvent (phosphoric and/or hydrochloric acid solutions) upon UV spectra of I and 3-acetylindole (3-AI) was examined. For determine the pK_a values, from the data obtained by analyzing the UV-spectra by any the characteristic vectors, it is possible to separate the medium effect from the larger changes due to the protonation.

Experimental

Stock solutions of I and 3-AI were prepared in a mixture of water and ethanol (1.0% v/v). More dilute solutions of I or 3-AI were prepared from solutions (by keeping the concentration of I (or 3-AI) constant), in different the concentrations of phosphoric acid (between 1.0 and 11.5 mol dm⁻³) and hydrochloric acid (between 1.0 and 8.0 mol dm⁻³). The concentration of I or 3-AI for UV-measurements was chosen in such a way that the absorbance had a value between 0.1 and 1.0 at the studied wavelength.

The UV spectra of each solution were recorded between 400 - 190 nm on a Hewlett-Packard 8452A Diode Array Spectrophotometer, in 1 cm quartz cells. A solution of phosphoric or hydrochloric acid (of the same concentration as in the investigated solutions) was used as a blank. The measurements were performed 1 - 1.5 min after preparing the solution at $27.0 \pm 0.2^\circ$ C in thermostated cell. From the absorbances on four selected experimental wavelengths, molar absorptivity (ϵ) of B and BH⁺ were determined (Table 1).

Table 1. Wavelengths and the corresponding molar absorptivity for I ($c = 3.1 \cdot 10^{-5} \text{ mol dm}^{-3}$) and 3-AI ($c = 4.010^{-5} \text{ mol dm}^{-3}$) in different solvents.

Compound	Solvent	$c / \text{mol dm}^{-3}$	λ/nm ($\log \epsilon / \text{mol}^{-1} \text{dm}^3 \text{cm}^{-1}$)			
			I	HCl	3.5 8.0	210 (4.42) (3.93)
	H ₃ PO ₄	3.5 11.0	204 (4.37) (4.00)	210 (4.47) (4.03)	216 (4.54) (4.00)	222 (4.41) (3.87)
3-AI	HCl	1.0 6.0	280 (3.91) (3.50)	300 (4.13) (3.81)	320 (3.76) (4.00)	340 (2.86) (4.03)
	H ₃ PO ₄	3.5 11.0	280 (3.85) (3.45)	300 (4.10) (3.84)	320 (3.80) (4.02)	340 (2.99) (3.98)

Results and discussion

1. UV spectra of indole in water and phosphoric acid and hydrochloric acid solutions

Since the indoles possess basic properties it is important to know exactly which ionic species are present under certain conditions. Kouzumi [25] has noted that in medium with $\text{pH} < 0.5$ zwitterionic tautomers (II) may be present (see Scheme 1).

It is known that UV spectrum of I in water exhibits four bands which result from $\pi \rightarrow \pi^*$ transitions [26]. In water solution the UV spectrum of I shows absorption maximum at: 196 nm ($^1\text{B}_a$), $\log\{\epsilon\} = 4.31$; 216 nm ($^1\text{B}_b$), $\log\{\epsilon\} = 4.49$; 270 nm ($^1\text{L}_a$), $\log\{\epsilon\} = 3.74$; 276 nm and 286 nm ($^1\text{L}_b$), $\log\{\epsilon\} = 3.73$ [15], [UV spectrum of I was assigned and interpreted using the FREE ELECTRON MODEL [26]]. Figure 1 shows ultraviolet spectra of I at different concentration of phosphoric acid solutions.

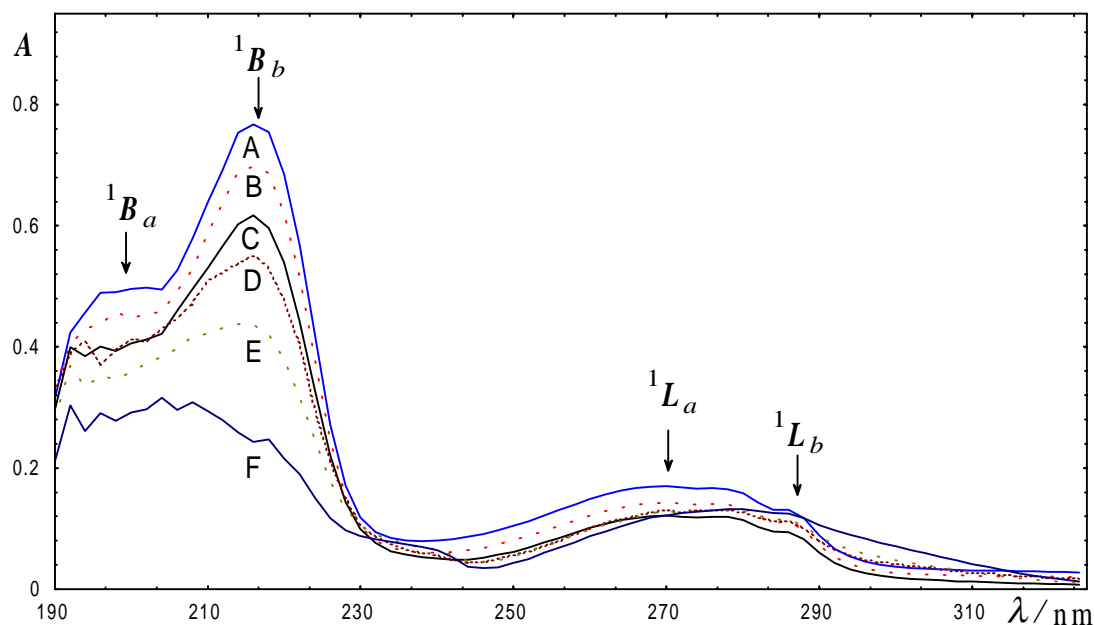


Figure 1. Ultraviolet absorption spectra of indole ($c = 3.1 \cdot 10^{-5} \text{ mol dm}^{-3}$ -A-in water) as a function of phosphoric acid concentration. The concentration of phosphoric acid: (B)-6.5; (C)-7.5; (D)-8.5; (E)-9.5 and (F)-10.5 mol dm^{-3} (top to bottom, at $\lambda = 216 \text{ nm}$).

In general, the solvents (perchloric acid solutions or sulfuric acid solutions) cause changes in the intensity of the 1B_a , 1B_b , 1L_a and 1L_b bands, in analytical concentration (above 1.0 mol dm^{-3}).^{11,13} On the other hand, in phosphoric acid solutions the changes in intensity of all four bands above analytical concentration 5.5 mol dm^{-3} (Fig.1.) are noted. The changes in the UV spectra of I observed in phosphoric acid are in agreement with those, which were observed in perchloric or sulfuric acid solutions.^{11,13} In Table 2 characteristic bands of the UV spectrum of IH^+ are listed.

Table 2. Experimental transitions in the UV spectra of IH^+

Ion IH^+ in solvents	$HClO_4$	H_2SO_4	$H_2SO_4^{15}$	H_3PO_4	HCl
Transitions	λ/nm				
1L_b	276	280	281	280	270
1L_a	—	—	—	—	—
	240(sh)	240(sh)	238	240(sh)	240(sh)
1B_b	232	234	233	232	234(sh)
1B_a	204	202	—	204	206(sh)

(sh)-shoulder

In phosphoric acid solutions at concentration higher than 5.5 mol dm^{-3} , the solvent influences on the shift of the absorption curves of I and causes loss of the isosbestic points (Fig.1). Figure 2 shows six curves reconstituted from the “mean” curve and first vector, using CVA.^{27,28}

Method of Characteristic Vector Analysis

Characteristic vector analysis (sometimes referred to as “principal component analysis” or eigenvector analysis) is a method of separating independent factors for sets of multivariate response data. The method can be used empirically for estimating the number of independent factors contributing to the total variation observed in a family of UV spectra. If p independent factors are involved in generating the absorbance curve, the sample responses at each wavelength for a given concentration will be given by

$$\begin{aligned} A_1 &= A_1 + c_1 V_{11} + c_2 V_{21} + \dots + c_p V_{p1} \\ A_2 &= A_2 + c_1 V_{12} + c_2 V_{22} + \dots + c_p V_{p2} \\ &\vdots \\ A_r &= A_r + c_1 V_{1r} + c_2 V_{2r} + \dots + c_p V_{pr} \end{aligned} \quad (1)$$

where the choice of A is arbitrary and the mean values of the absorbance seem to be a convenient choice. The V 's are characteristic vectors, and c 's are weighting coefficients.

Ultraviolet spectra of I in solutions of different concentration of phosphoric acid $>5.5 \text{ mol dm}^{-3}$, show isosbestic points at 236 and 288 nm. For comparison, isobestic points of 238 and 288 nm in UV spectra of I in sulfuric acid solutions and perchloric acid solutions 234, 244 and 288 nm are obtained. The agreement of these results indicate that CVA method can be used for determination of isobestic points.

Reeves [29] reported, that have only two characteristic vectors. The first vector can be used in CVA to obtain always accounted for 96% or more of the total variability. The physical-chemical meaning of the first vector associate with the effect of the protonation and second vector with the medium effect. By application the CVA the family ten UV spectra of indole in phosphoric acid solutions calculation of the first vector accounts for 97.5%, meaning that the protonation effect prevails the medium effects.

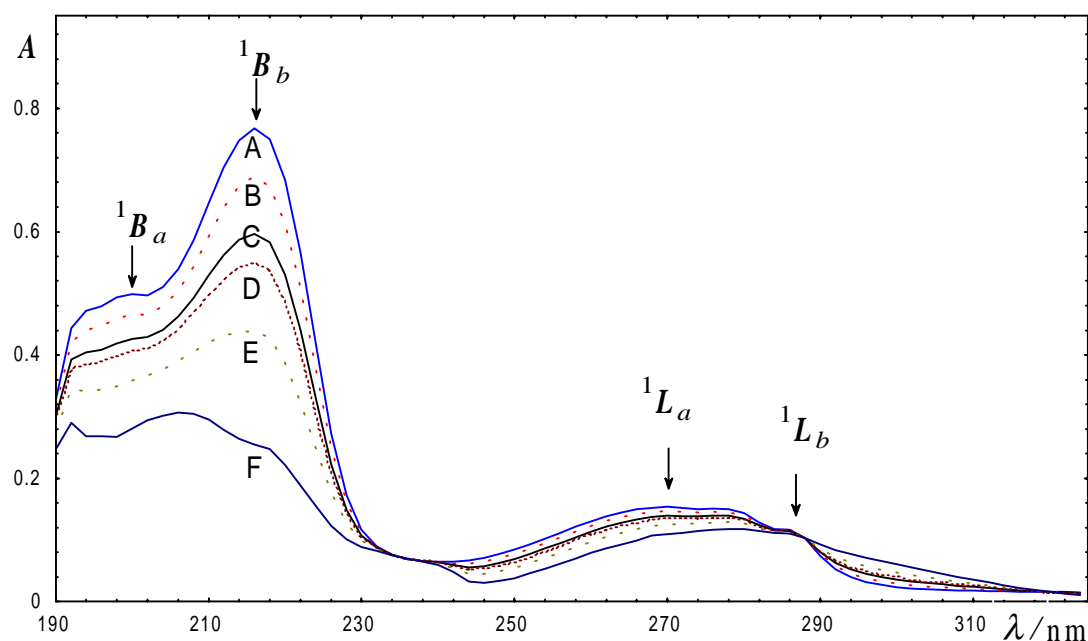
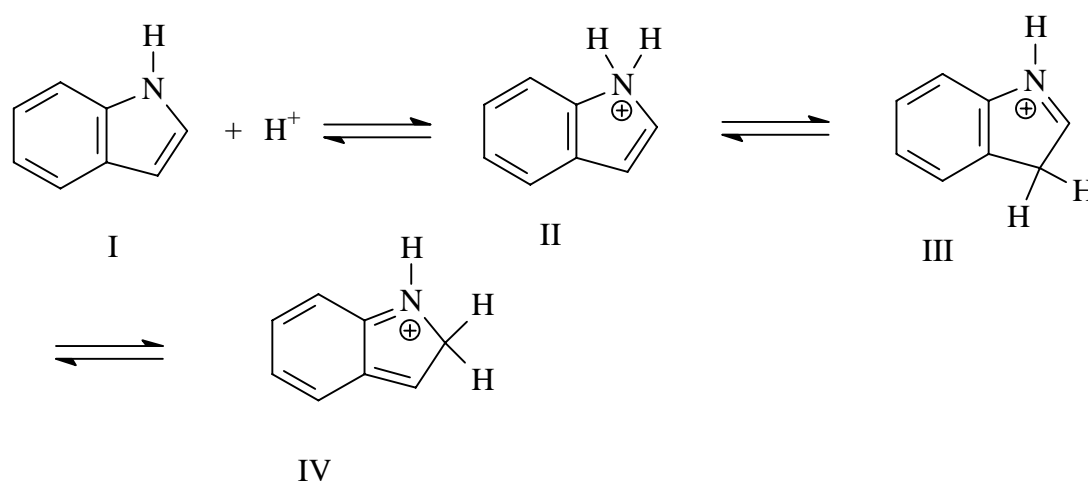


Figure. 2. The reconstituted UV spectra of indole ($c = 3.1 \cdot 10^{-5} \text{ mol dm}^{-3}$, A-in water) as a function of concentration phosphoric acid. From top to bottom: B- 6.5 mol dm^{-3} ; C- 7.0 mol dm^{-3} ; D- 7.5 mol dm^{-3} ; E- 8.5 mol dm^{-3} and F- 9.5 mol dm^{-3} .

Two isosbestic points at 238 and 288 nm obtained in UV spectra of I in sulfuric acid solutions are in agreement with the results obtained in phosphoric acid solutions. The wavelengths of the isosbestic points obtained for I in perchloric acid solutions do not agree with those in phosphoric or sulfuric acid.

In UV spectrum of I in a phosphoric acid solution with concentration 11.5 mol l^{-3} there are absorption maxima at 204 (1B_a), 232 (1B_b) and a broad absorption band at 280 (1L_b) nm (Fig.1). This absorption spectrum of IH^+ was compared to the spectra of IH^+ in perchloric acid solution and sulfuric acid solution (Table 2). It is possible therefore, that the protonation of I is leading to the 3-C atom (structure III), and IH^+ cannot have structures II or IV (See scheme 1).



Scheme 1

UV spectra of indole in hydrochloric acid solutions

The observed changes in the UV spectrum of I in hydrochloric acid solutions (from 1.0 to 10.0 mol dm⁻³) are similar to those previously published for perchloric and sulfuric acid solutions.^{11,13} In hydrochloric acid solutions with the concentration higher than 1.0 mol dm⁻³, a medium effect on the absorption curves causes loss of the isosbestic points. The application of the CVA method, for ten UV spectra of I in hydrochloric acid solutions is resulting in appearance of two isosbestic points at 236 and 292 nm. The first vector accounts for 91.6 % of the variability. It is possible, that 3-C atom is protonated in this case of (See sheme 1 - structure III). Podkovinska et al.¹⁶ observed two bands in UV spectrum of the protonated form of I in sulfuric acid at wavelengths at 258 and 262 nm. In this work, in UV spectra of I at concentration of phosphoric acid from 10.5 to 11.5 mol dm⁻³ and hydrochloric acid solutions 7.5 to 8.5 mol dm⁻³, bands at wavelengths about 260 nm are not obtained.

Similarly, in UV spectra of I in sulfuric acid solution or perchloric acid solutions, bands at $\lambda > 260$ nm in this region are not obtained.^{11,13} Therefore, it is possible, that the new bands appearing at 258 and 262 nm result from the formation of a new reaction product during the process of protonation (isomerization or oxidation of protonated form of I).

2. UV spectra of 3-acetylidole in water, in phosphoric acid and hydrochloric acid solutions

Figure 3 shows six UV spectra of 3-AI in water and phosphoric acid solutions at concentration from mol dm^{-3} to mol dm^{-3} . UV spectrum of 3-AI shows in water media absorption maxima at: 206 nm (1B_a), $\log \{\epsilon\} = 4.38$; 242 nm (1B_b), $\log \{\epsilon\} = 4.02$; 260 nm (1L_a), $\log \{\epsilon\} = 3.93$; 300 nm (1L_b), $\log \{\epsilon\} = 4.03$. Changes in the UV spectrum of 3-AI (1B_a , 1B_b , 1L_a and 1L_b bands) in phosphoric acid solutions in the concentration range from 4.5 to 11.0 mol dm^{-3} are noticeable, of similar for those in perchloric or sulfuric acid solutions.^{12,14} UV spectra of 3-AI in phosphoric acid solutions are not showing isosbestic points, indicating the solvent influence within the used range of phosphoric acid concentrations.

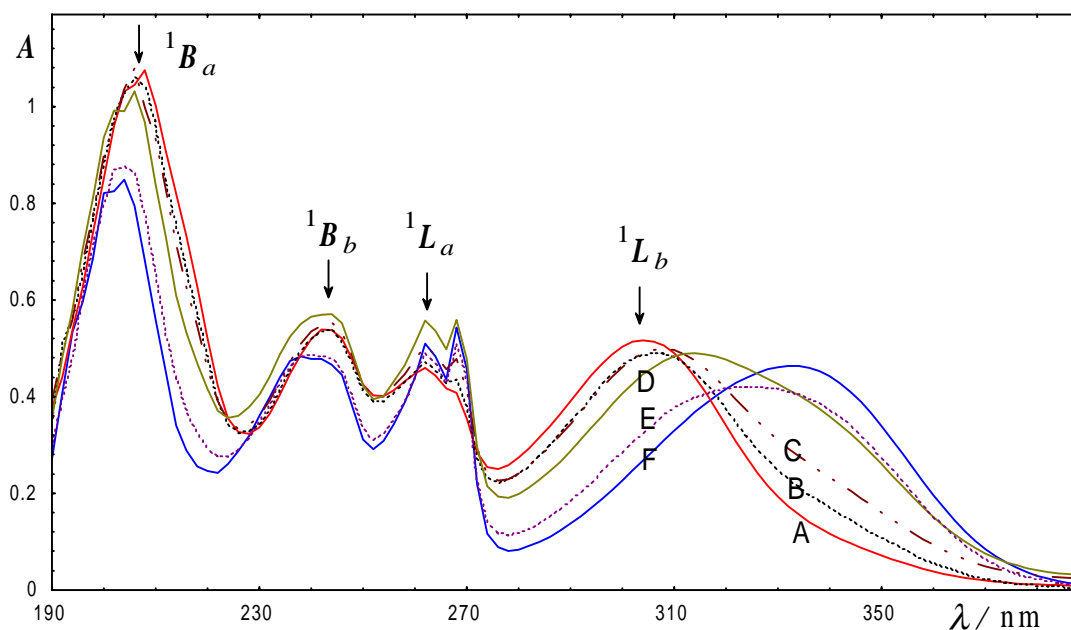


Figure 3. Ultraviolet absorption spectra of 3-acetylidole ($c = 4.0 \cdot 10^{-5} \text{ mol dm}^{-3}$) as a function of phosphoric acid concentration. From top to bottom, at wavelengths 300 and 340 nm): B-4.5 mol dm^{-3} ; C-5.5 mol dm^{-3} ; D-6.5 mol dm^{-3} ; E-7.0 mol dm^{-3} and F-7.5 mol dm^{-3} .

The wavelengths of the isosbestic points for UV spectra of 3AI in phosphoric acid 228, 238, 260, 270 and 316 nm are obtained (Fig. 4). From comparison of the wavelengths of isosbestic points, using CVA method for ten UV spectra of 3-AI in perchloric acid solutions (230, 236, 258, 272 and 314 nm)¹² or sulfuric acid solutions

(226, 242, 260, 270 and 316 nm)¹⁴ it may be concluded that the same reaction of protonation is observed.

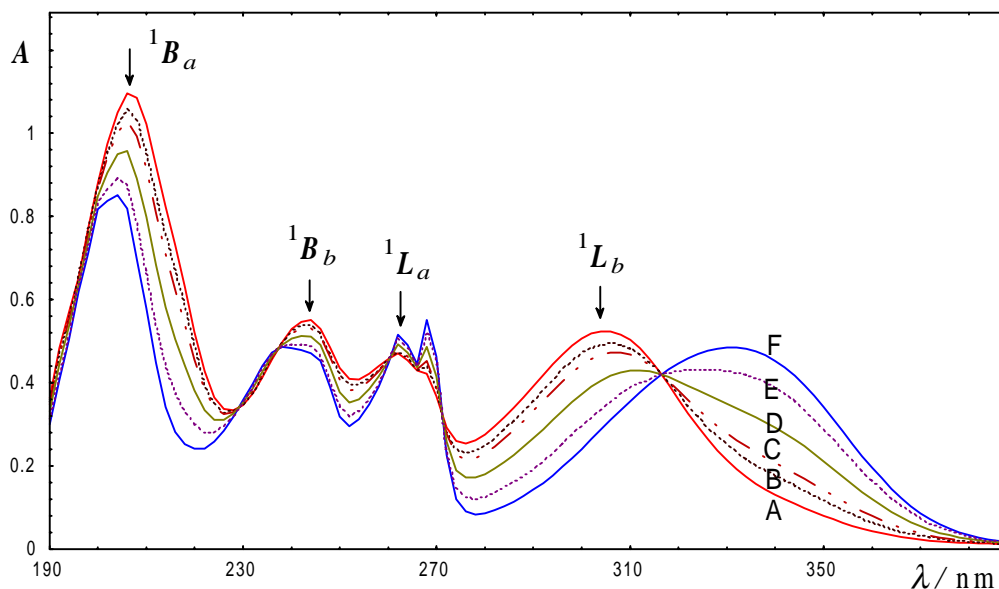


Figure. 4. The reconstituted UV spectra of 3-AI ($c = 4.0 \cdot 10^{-5} \text{ mol dm}^{-3}$, A-in water) as a function of concentration of phosphoric acid. From top to bottom: B- 4.5 mol dm^{-3} ; C- 5.5 mol dm^{-3} ; D- 6.5 mol dm^{-3} ; E- 7.0 mol dm^{-3} and F- 7.5 mol dm^{-3} .

UV spectrum of IH^+ in phosphoric acid solution [Fig.5(A)] was compared with spectrum of 3-AIH^+ in phosphoric acid solution [Fig.5(B)]. In UV spectrum of 3-AIH^+ (protonated form) band at 280 nm is not present. Therefore, formation of species (II) (See scheme 2) is not appearing and this comparison clearly indicates that formation of species (V) is obtained.

In UV spectra of 3-AI in hydrochloric acid solutions (from 1.0 to 8.0 mol dm^{-3}) date of the isosbestic points has not been observed. Changes of ${}^1\text{B}_a$, ${}^1\text{B}_b$, ${}^1\text{L}_a$ and ${}^1\text{L}_b$ bands are analogous to those obtained in UV spectra of 3-AI in perchloric acid,¹² sulfuric acid¹⁴ and phosphoric acid solutions. In this case, wavelengths of isosbestic points at 240, 258, 272 and 316 nm are observed. The UV spectra of IH^+ and 3-AIH^+ are in fact significantly different (Fig.5, curve A and curve B). From this case it was shown that 3-AIH^+ couldn't exist in structure (II), see Scheme 2. The observed transitions of the UV spectra of 3-AIH^+ are shown in Table 3.

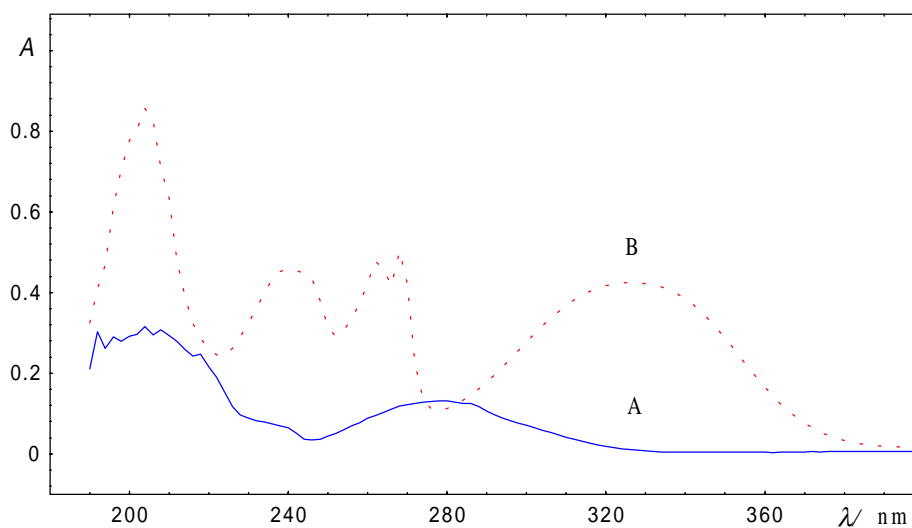
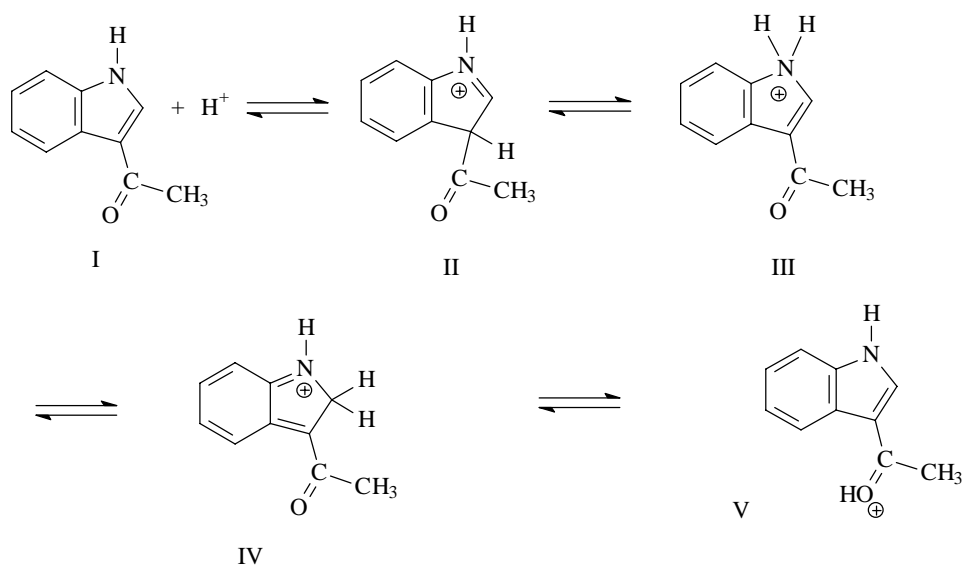


Figure 5. Comparison of UV spectra of indole ($3.1 \cdot 10^{-5} \text{ mol dm}^{-3}$) in phosphoric acid solution (11.5 mol dm^{-3}) - curve A, and 3-acetylindole ($4.0 \cdot 10^{-5} \text{ mol dm}^{-3}$) in phosphoric acid solution (9.5 mol dm^{-3}) - curve B

Table 3. Experimental transitions in the UV spectra of 3-AIH⁺ in different solvents

Ion 3-AIH ⁺ in solvents	HClO ₄ ¹²	H ₂ SO ₄ ¹⁴	H ₃ PO ₄	HCl
Transitions	λ/nm			
¹ L _b	340	338	326	334
¹ L _a	262, 268	262, 268	262, 268	262, 268
¹ B _b	236	236	240	240
¹ B _a	202	200	204	210

Determination of pK_a values with HAFM and EAM

pK_a values are calculated, using, equations (2) .

$$\text{pK}_a(H_0) = H_0 + \log I \quad (2)$$

$$H_0 = -\log \frac{a(\text{H}^+) \cdot f(\text{B})}{f(\text{BH}^+)} \quad (3)$$

$$-H_0 = -\log c(\text{H}^+) + \log f(\text{H}^+) + \log f(\text{B}) - \log f(\text{BH}^+) \quad (4)$$

On different concentration of mineral acid H_0 are obtained.³⁰

H_0 -is Hammett Acidity Function.³⁰

In order to determine the ionization ratio $\log I$ or $\log c(\text{BH}^+)/c(\text{B})$ in Hammett's equation (2) the absorbance was measured at four analytical wavelengths (Table 1). Concentrations of the protonated $c(\text{BH}^+)$ and unprotonated $c(\text{B})$ forms were obtained by solving the system of linear equations:

$$A_{\lambda 1} = \varepsilon_{\lambda 1}(\text{B}) c(\text{B}) + \varepsilon_{\lambda 1}(\text{BH}^+) c(\text{BH}^+) \quad (5)$$

$$A_{\lambda 2} = \varepsilon_{\lambda 2}(\text{B}) c(\text{B}) + \varepsilon_{\lambda 2}(\text{BH}^+) c(\text{BH}^+)$$

$$A_{\lambda 3} = \varepsilon_{\lambda 3}(\text{B}) c(\text{B}) + \varepsilon_{\lambda 3}(\text{BH}^+) c(\text{BH}^+)$$

$$A_{\lambda 4} = \varepsilon_{\lambda 4}(\text{B}) c(\text{B}) + \varepsilon_{\lambda 4}(\text{BH}^+) c(\text{BH}^+)$$

In this work for determination of pK_a values $H_0(\text{H}_2\text{SO}_4)$, $H_0(\text{HClO}_4)$, $H_0(\text{H}_3\text{PO}_4)$ [and $H_0(\text{HCl})$ have been used.³¹

Values of pK_a and m^* (is related with the stabilization of acid-base conjugated pair by solvation) for IH^+ and 3-AI are obtained using eq. (6)

$$\log I - \log c(H^+) = \log \frac{f(H^+) \cdot f(B)}{f(BH^+)} + pK_a \quad (6)$$

$$\log \frac{f(H^+) \cdot f(B)}{f(BH^+)} = m^* \cdot \log \frac{f(H^+) \cdot f(Am)}{f(AmH^+)} \quad (7)$$

$$\log I - \log c(H^+) = m^* \cdot X + pK_a \quad (8)$$

In this work, however, equation:

$$-X = H_0 + \log c(H^+) \quad (9)$$

is useful for calculation of X values.

Values of X are available for aqueous H_2SO_4 , $HClO_4$ and HCl .³¹ Values of $\log c(H^+)$ for hydrochloric acid solution are simply the \log acid molarities for fully dissociated acid. To calculate the values of $\log c(H^+)$ in phosphoric acid solutions the equation (10) was used.

$$c(H^+) = \sqrt{c(H_3PO_4) \cdot K_{a1}} \quad (10)$$

Conclusions

The results in Table 4 show that pK_a values for indole obtained in hydrochloric or phosphoric acid solutions are in good agreement with the values for I in perchloric or sulfuric acid solutions.

In this case different values of the H_0 scale does not introduce large errors. Our $pK_a(H_0)$ values for 3-AI obtained for phosphoric or hydrochloric acid solutions do not agree with application at perchloric or sulfuric acid solutions (Table 4).

This difference is an error that is not so much important for many purposes. In the Table 4 we have also included results from literature for pK_a values of I, and for comparison purposes we have included $pK_a(X)$ values obtained using EAM.

Table 4. pK_a values for indole and 3-acetylindole

Ions	Solvents	$-pK_a(H_o)$	$-pK_a(X)^a$	m^*
IH^+	HClO ₄	2.6 ± 0.2^{11}	3.0 ± 0.20	1.1 ± 0.10
	H ₂ SO ₄	2.8 ± 0.2^{13} $4.74^{16}; 3.50^{15};$ 2.4^{24}	2.2 ± 0.18	0.8 ± 0.10
	HCl	3.0 ± 0.2	2.1 ± 0.15 (0.9832) ^b	0.4 ± 0.10
	H ₃ PO ₄	2.5 ± 0.2	3.1 ± 0.60 (0.9859)	1.1 ± 0.01
$3-AIH^+$	HClO ₄	1.8 ± 0.1^{12}	1.2 ± 0.40	0.6 ± 0.10
	H ₂ SO ₄	1.7 ± 0.2^{14}	1.3 ± 0.10	0.8 ± 0.10
	HCl	1.3 ± 0.1	1.5 ± 0.08 (0.9849)	1.3 ± 0.10
	H ₃ PO ₄	1.5 ± 0.1	1.3 ± 0.09 (0.9911)	0.9 ± 0.05

^aObtained by the least squares treatment of $\log I - \log c(H^+)$ vs. X

^bThe number in parentheses is the correlation coefficient

The more relevant difference in $pK_a(X)$ values is observed in the case of indole protonation in hydrochloric acid solution. A comparison of the $pK_a(X)$'s obtained from EAM with appropriate HAFM for 3-AI using phosphoric or hydrochloric acid solutions reveals as satisfactory correspondence.

In Table 4 are also included the results of a second m^* parameter, which is related with the solvation requirements of the acid-base conjugate pair. The m^* values for protonation of I or 3-AI in perchloric acid, sulfuric acid, phosphoric acid and hydrochloric acid solutions can be interpreted with the structure of the protonated forms. In protonated form of I presence in perchloric or phosphoric acid involve a large localization of their positive charge on nitrogen atom 1-N. The m^* values of protonated form of 3-AI are in very good agreement with its behavior as a O-base.

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Povzetek

Z UV spektroskopijo smo študirali protonacijo 3-acetilindola v raztopinah fosforne in solne kisline. pK_a smo izračunali z uporabo CVA (Characteristic Vector Analysis) metode. pK_a vrednosti za protonacijo smo izračunali z uporabo Hammettove enačbe: $pK_a = H_0 + \log[c(\text{BH}^+)/c(\text{B})]$. Disociacijske konstante in parameter m^* smo dobili z uporabo Excess Acidity Method. Na osnovi rezultatov smo določili mesto protonacije.