

Spectrophotometric study of the protonation processes of some indole derivatives in sulfuric acid

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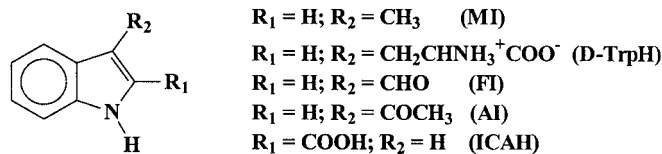
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The protonation of 3-methylindole, D-tryptophan, 3-formylindole, 3-acetylindole and indolyl-2-carboxylic acid in sulfuric acid media was studied by UV spectroscopy. The measurement of the absorbance at four selected wavelengths enabled the calculation of the corresponding molar absorptivities. The results were used to calculate the pK_a value of the protonated form of the indole derivatives by the Hammett Method. The Hammett postulate (the slope of the plot $\log [c(\text{BH}^+)/c(\text{B})]$ vs. H should be equal to 1) was tested. The dissociation constants and solvent parameter m^* were also obtained by applying the Excess Acidity Method. The position of the additional protons in the protonated compounds is discussed.

Keywords: 3-methylindole, D-tryptophan, 3-formylindole, 3-acetylindole, indolyl-2-carboxylic acid, protonation, dissociation constants, solvent parameter, Hammett Acidity Function Method, Excess Acidity Method.

It has been known for some time that the UV spectra of indole and a number of its derivatives, both naturally occurring and synthetic, depend on the acidity of the solutions in which they were measured.¹⁻³ Some indoles are used as acid/base indicators.⁴⁻⁷ Of the indole derivatives studied in this work only the behavior of 3-methylindole in sulfuric acid has been the subject of investigation of Berti *et al.*⁶ and Hinman *et al.*⁷ Literature data⁸ on the bromination of some simpler 3-substituted indoles, such as 3-methylindole (skatole) and 3-(3-indolyl)propionic acid, show that protonation of the indole is the first step in this reaction. Knowledge of the pK_a values is, therefore, very useful in the study of organic reaction mechanisms in this non-ideal strong acid system.^{9,10} In the course of our systematic investigation^{11,12} of the acid-base properties of indole derivatives, we deemed it might be of interest to study the behavior of 3-methylindole (MI), D-tryptophan (D-TrpH), 3-formylindole (FI), 3-acetylindole (AI) and indolyl-2-carboxylic acid (ICAH) in sulfuric acid media.

The purpose of the present work was to determine the dissociation constants (pK_a) using the Hammett Acidity Function Method (HAFM)¹³ and the Excess



Acidity Method (EAM),^{14–16} which have been successfully employed in the determination of pK_a values from spectral measurements, in the presence of medium effects. In addition, the exact positions of protonation have been inferred from the values of the solvation parameters (m^*) and the order of the protonation of these compounds.

The studied compounds proved to be unstable in sulfuric acid solution, as evidenced by the time-dependent changes in their UV spectra.⁷ In these cases, the time dependence of the absorbance at $\lambda = 222$ nm was recorded and the value for $t = 0$ was obtained by linear extrapolation. By using a HP8452A Diode Array Spectrophotometer, which is much faster (the scan time per full spectrum scan is about 0.1 s) than other conventional instruments, the method of linear extrapolation could be abandoned.

The ions formed in the protonation reaction of MI and D-TrpH are kinetically unstable compounds, so the rate of sample scanning is important. It is necessary to examine the protonation of MI, D-TrpH, FI and AI in the proton donor sulfuric acid. In such a medium sulfonation is also possible, which leads to errors during the determination of the dissociation constants.

EXPERIMENTAL

Reagents

3-Methylindole (MI), D-tryptophan (D-TrpH), 3-formylindole (FI), 3-acetylindole (AI), and indolyl-2-carboxylic acid (ICAH) were Merck products and were used without further purification. The physical properties of these compounds (UV absorption spectra and infrared spectra) were in good agreement with the literature values. The purity of MI was further checked by gas-chromatography, on PERKINELMER GC-F17 instrument equipped with a hydrogen flame ionization detector.

Reagent grade sulfuric acid (97% by weight, product of Alkaloid-Skopje) was used. The concentration of the sulfuric acid was determined by titration with sodium hydroxide.

Stock solutions (1 mmol/dm^3) were prepared from MI, D-TrpH, FI, AI and ICAH in a mixture of water and ethanol (10% by volume). Other more diluted solutions were prepared from these solutions and different concentration of sulfuric acid (from 0.1 to 17.0 mol/dm^3). The degree of dilution of the solutions was chosen in such a way that the absorbance had a value between 0.1 and 1.0 at the studied wavelength.

UV absorption spectra

The UV spectra of each solution were recorded on a Hewlett-Packard 8452A Diode Array Spectrophotometer. The absorbances were measured in 1 cm quartz cells at four analytical wavelengths (Table I). A solution of sulfuric acid (of the same concentration as in the investigated solution) was used as a blank. The spectra were recorded 1–1.5 min after preparation of the solution at $27 \pm 0.2^\circ \text{C}$ in a thermostated cell.

TABLE I. Wavelengths with (molar absorptivity) in sulfuric acid solutions of all the studied compounds (3-methylindole, D-tryptophan, 3-formylindole, 3-acetylindole and indolyl-2-carboxylic acid) used for dissociation calculations

Cpd.	$c(\text{H}_2\text{SO}_4)/\text{mol}/\text{dm}^3$	$1/\text{nm}$ and $\log(\epsilon/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1})$			
MI	1.0	200 (4.19)	210(4.18)	222(4.46)	232(4.02)
	9.5	(3.62)	(3.58)	(3.64)	(3.69)
D-TrpH	6.0	208(4.22)	214(4.30)	220(4.32)	226(4.13)
	11.0	(3.56)	(2.96)	(2.96)	(3.20)
FI	1.0	300(3.88)	310(3.80)	320(3.53)	330(3.13)
	8.0	(3.41)	(3.62)	(3.76)	(3.82)
AI	1.0	280(3.75)	300(4.00)	320(3.62)	340(2.65)
	9.5	(3.14)	(3.41)	(3.93)	(4.14)
ICAH	12.0	300(4.06)	310(4.04)	320(3.91)	330(3.70)
	17.0	(3.53)	(3.71)	(3.82)	(3.83)

RESULTS AND DISCUSSION

UV spectra and protonation of the 3-methylindole, D-tryptophan and indole-2-carboxylic acid in sulfuric acid solutions

The UV spectra of MI and D-TrpH dissolved in water are very similar, exhibiting four bands (Table II), resulting from $\pi \rightarrow \pi^*$ transitions in the indolic ring. The position and intensity of all the indole bands are influenced by the presence of a methyl group in the indolic ring. Due to the inductive effect of the methyl group, very small changes in the positions/intensities of the indole bands arise (Table II). When a hydrogen atom in the methyl group is replaced by the $-\text{CHNH}_3^+\text{COO}-$ group, the bathochromic effect decreases. This is illustrated in Table II, which shows the wavelength of the ${}^1\text{B}_a$, ${}^1\text{B}_b$, ${}^1\text{L}_a$ and ${}^1\text{L}_b$ transitions in the spectra of the investigated indoles. This indicated that the $-\text{CH}_2\text{CHNH}_3^+\text{COO}-$ group behaves as a weaker σ -donor than the methyl group.

The changes in the spectra of MI and D-TrpH in the concentration range 1.0 to 11.0 mol/dm^3 H_2SO_4 are analogous. The behavior of MI and D-TrpH in sulfuric acid solutions is similar to that of indole, 2-(3-indolyl)acetic acid, 3-(3-indolyl)propionic acid and 4-(3-indolyl)butyric acid.¹⁹ The UV absorption spectra of D-TrpH at different acidities are illustrated in Fig. 1. The changes in the UV spectra probably result from the formation of the protonated ions: D-TrpH_2^+ (cation of D-tryptophan) and MIH^+ (cation of 3-methylindole), see Scheme 1. The observed transitions of the UV spectra of D-TrpH_2^+ and MIH^+ are shown in Table III.

The bands at 290 and 292 nm (Table III) in the spectra, probably of D-TrpH_2^+ and MIH^+ ions, respectively, are due to the intramolecular charge-transfer transition from the Highest Occupied Molecular Orbital (HOMO) of one part of the ion (the phenylene ring), which acts as an electron-donor, to the Lowest Unoccupied

Molecular Orbital (LUMO) of the other part (iminium group), which serves as an electron acceptor.

TABLE II. Electronic transitions in water solutions. Concentrations of the compounds in water were $4 \cdot 10^{-5} \text{ mol/dm}^3$

Compounds	$1/\text{nm}$	$\log \epsilon/\text{mol}^{-1} \text{dm}^3 \text{cm}^{-1}$	Transitions
MI	198	4.25	$1B_a$
	222	4.45	$1B_b$
	280	3.70	$1L_a$
	288(sh)	3.67	$1L_b$
D-TrpH	200	4.25	$1B_a$
	218	4.45	$1B_b$
	280	3.70	$1L_a$
	288(sh)	3.66	$1L_b$
FI	208	4.37	$1B_a$
	244	4.06	$1B_b$
	262	4.03	$1L_a$
	300	4.07	$1L_b$
AI	208	4.38	$1B_a$
	242	4.202	$1B_b$
	260	3.93	$1L_a$
	300	4.03	$1L_b$
ICAH	202	4.23	$1B_a$
	218	4.26	$1B_b$
	292	4.22	$1L_a 1L_b$

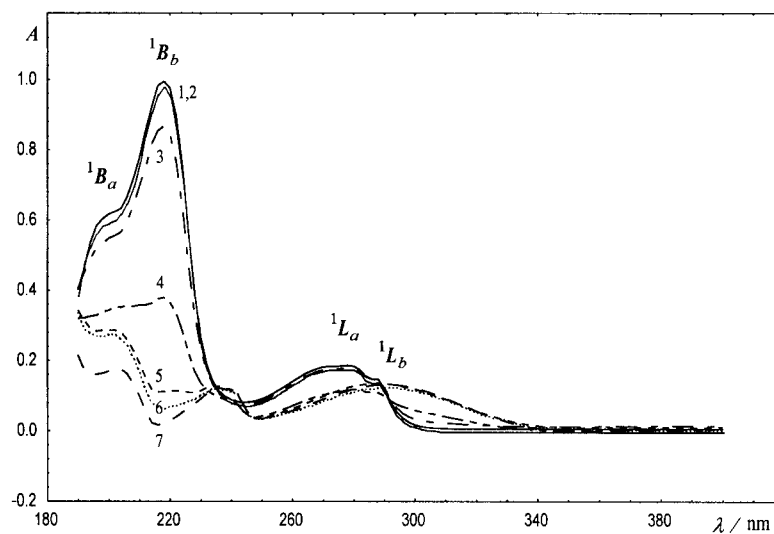


Fig. 1. UV spectra of D-tryptophan ($c = 4.0 \cdot 10^{-5} \text{ mol/dm}^3$) as a function of sulfuric acid concentration (mol/dm^3): 6.0(1); 7.0(2); 8.0(3); 8.5(4); 9.5(5); 10.5(6) and 11.0(7).

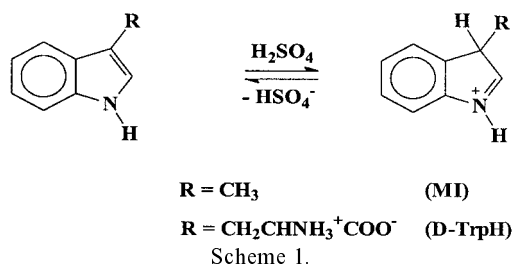
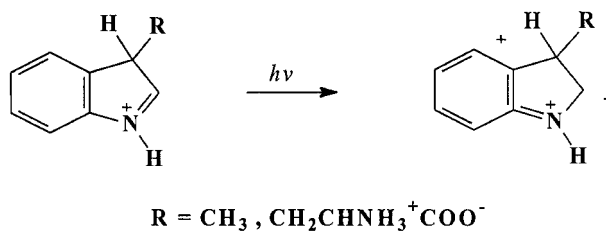


TABLE III. Experimental transitions in water solutions. Concentrations of the comopounds in water were $4 \cdot 10^{-5} \text{ mol dm}^{-3}$

Ions	MIH ⁺	D-TrpH ⁺²	FIH ⁺	AIH ⁺	ICAH ₂ ⁺
Transitions	l/nm				
¹ L _b	292 295.5*	290	332	338	332
¹ L _a	240 255*, 240*	240(sh)	262, 268	262, 268	238
¹ B _b	234 231*	236	236	236	230(sh)
¹ B _a	206	204	200	202	200

*Date of IAAH₂⁺, from Ref. 25

On the other hand, the shorter wavelength bands are probably due to transitions appearing at 206 and 234 nm for MIH⁺ and 204 and 236 nm for D-TrpH₂⁺ within the phenylene ring. The UV absorption corresponding to the intramolecular charge-transfer transition may be represented by the following Scheme 2.



As illustrated in Fig. 1, the fact that the two absorption spectra intersect at a few points which are not common to all the other spectra must mean that either more than two forms or reaction products of the solute are present or that the change in conditions, for instance in acidity, which produces the variation in the proportion of the two forms also changes their molar absorptivity.²¹

The application of the Characteristic Vector Analysis (CVA)²² for separating these factors is therefore justified. The spectra, reconstituted according to Eq. (1) using only

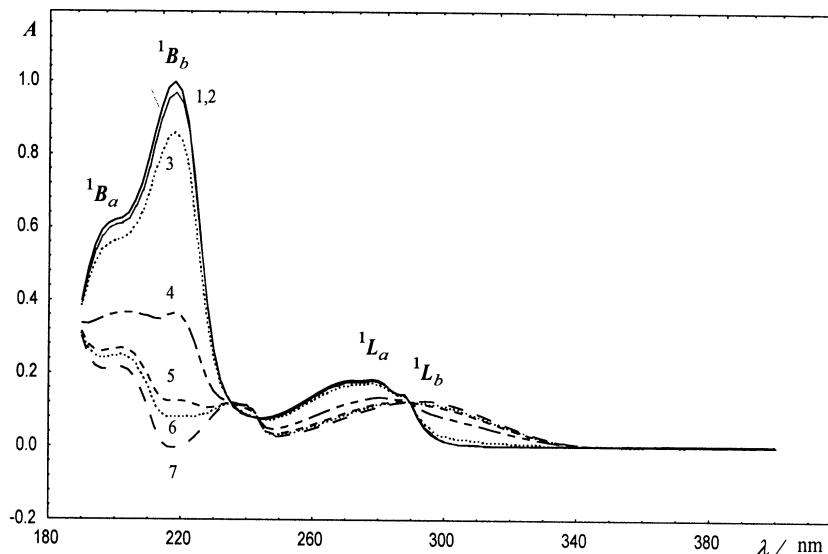
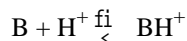


Fig. 2. UV spectra reconstituted from the mean curve and the first characteristic vector of D-tryptophan ($4.0 \cdot 10^{-5}$ mol/dm³) as a function of sulfuric acid concentration (mol/dm³): 6.0(1); 7.0(2); 8.0(3); 8.5(4); 9.5(5); 10.5(6) and 11.0(7).

$$A_1 = A_1(\text{mean}) + c_1 v_{11} + c_2 v_{21} \quad (1)$$

A_1 (mean), n_{11} , n_{21} ... (characteristic vectors) and c_1, c_2 ... (weighing coefficients), show excellent isobestic points. The reconstituted spectra are shown in Fig. 2, from which it can be seen that all pass through a few isobestic points (at 235, 243 and 290 nm).

This is another strong indication that the first characteristic vector is indeed due to the effect of protonation. One may, therefore, be dealing with a single equilibrium:



The plot of absorbance (measured at $\lambda = 220$ nm) vs. the H_i acidity function of H₂SO₄ for D-TrpH gives a nonlinear curve (cf. Fig. 3), indicating a decrease in the concentration of the unprotonated form (in the range of -4.5 to $-6.5 H_i$). A similar curve was also obtained but, for MI in this case, the changes in the concentration of the unprotonated form are observed in the range of -3.5 to $-5.5 H_i$.

The UV spectrum of ICAH recorded in water exhibits four bands (Fig. 4). The position and intensity of these bands are in a good agreement with the literature data.²³ All these bands are due to $\pi \rightarrow \pi^*$ transitions. The bands were denoted 1B_a , 1B_b , 1L_a and 1L_b in the light of the free-electron model²⁰ (see Table II). The UV spectra of ICAH were measured in aqueous sulfuric acid solutions in the concentration range from 1.0 to 17.0 mol/dm³.

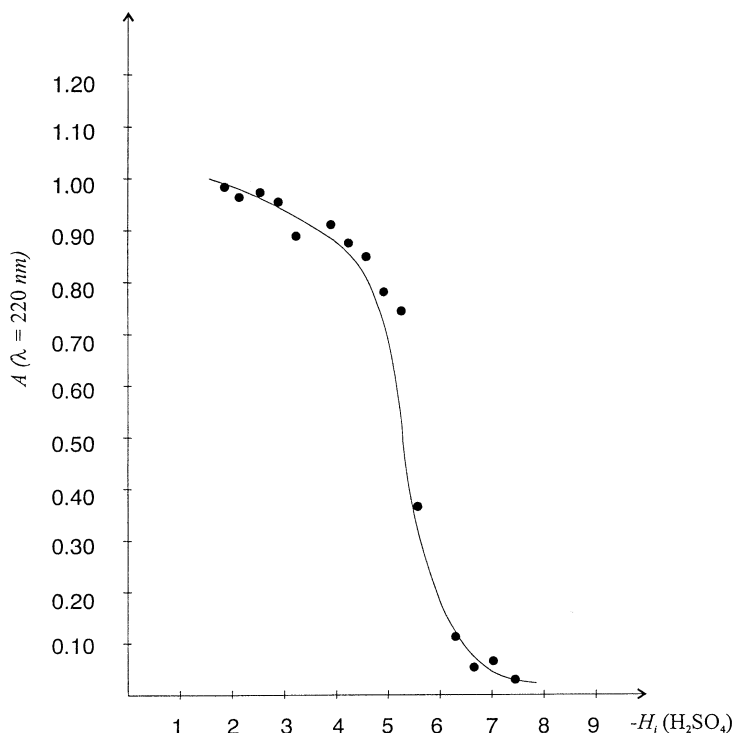


Fig. 3. Effect of the indolic acidity function H_i for sulfuric acid on the absorbance at 220 nm of D-tryptophan.

With increasing the concentration of the mineral acid, the intensities of the ${}^1\text{B}_a$ and ${}^1\text{B}_b$ bands decrease, showing at the same time red shifts,²⁰ in agreement with the literature data.²⁴ When this compound was investigated in more concentrated solutions (*i.e.*, 12.0 to 17.0 mol/dm³ H₂SO₄), pronounced changes occurred. Namely, in the long-wavelength region, the ${}^1\text{L}_a$, ${}^1\text{L}_b$ bands shift to 332 nm and decrease in intensity. The observed transitions in the UV spectrum of ICAH_2^+ are shown in Table III. This Table, for purposes of comparison, also includes literature data²⁵ for the calculated and experimentally found transitions in the UV spectrum of the cation of 2-(3-indolyl)carboxylic acid.

UV spectra and protonation of 3-formylindole and 3-acetylindole in sulfuric acid solutions

Groups, such as, $-\text{CHO}$, $-\text{COOH}$, $-\text{COCH}_3$, $-\text{CO}$ and others with n and p electrons can donate these electrons to the indolic ring, and this delocalization (resonance) induces shifts in the positions of the indole bands (*cf.* Table II). The spectra of MI and D-TrpH are very different from those of FI and AI recorded under same conditions (for positions and intensities of the observed bands *cf.* Table II). Also, no changes in the UV spectrum have been observed when a hydrogen atom

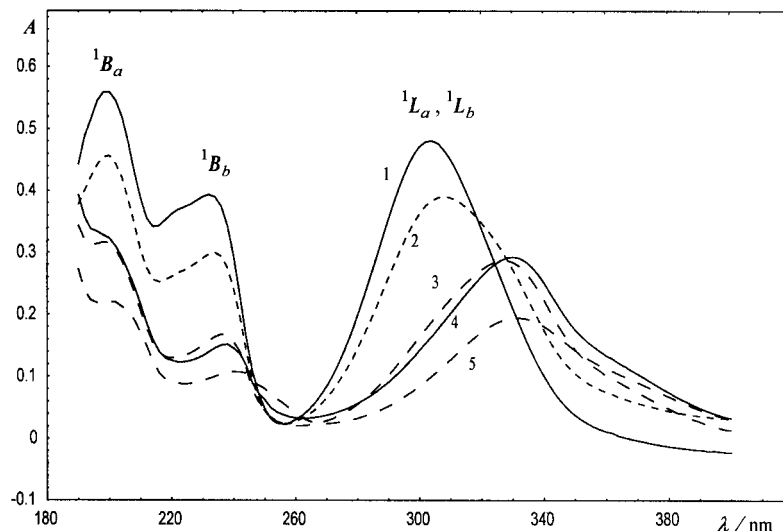


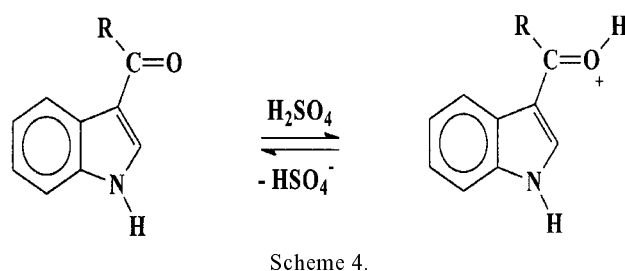
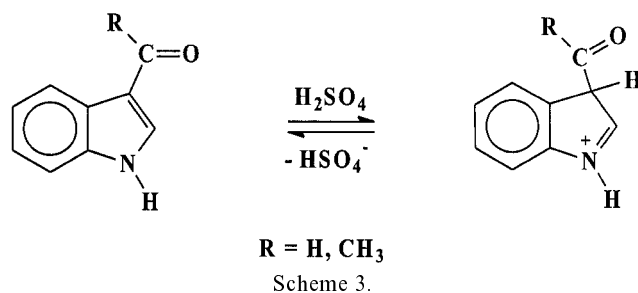
Fig. 4. UV absorption spectra of indolyl-2-carboxylic acid ($4.0 \cdot 10^{-5}$ mol/dm³) as a function of sulfuric acid concentration (mol/dm³): 12.0(1); 12.5(2); 14.0(3); 14.5(4) and 17.0(5).

from the aldehyde group is substituted by a methyl group. The changes in the spectra of FI and AI are analogic in the concentration range of 1.0 to 10.0 mol/dm³ H₂SO₄.

Increasing in the polarity of the solvent results in a bathochromic shift of the ¹L_b bands. The ¹L_b band of FI and AI disappear in sulfuric acid with a concentration of 7.5 mol/dm³. In both cases, new bands at 202 (¹B_a), 236 (¹B_b) and 262, 268 (¹L_a) nm appeared. Differences are observed in the position of the ¹L_b bands, 332 nm for ICAH⁺ (cation of 3-formylindole) and 338 nm for AIH⁺ (cation of 3-acetylindole). These differences, probably result from solvation changes. The band at 338 nm is probably due to the intramolecular charge-transfer transition from the indolic ring to the protonated carbonyl group.

On the basis of the above results, for both compounds, it seems that protonation lowers the energy of the ground state more effectively than that of the excited state. In the concentration region between 1.0 mol/dm³ and 9.0 mol/dm³, a doublet of bands appears at 262 and 268 nm. The splitting (the difference is 6 nm, corresponding to ≈ 850 cm⁻¹) may be associated with one of the out-of-plane C–H bending modes in the indolic ring. This doublet was also observed in spectra of these compounds in perchloric acid.¹² In this case, it may be of interest to discuss the various possible positions of protonation. The absence of the two conjugated fragments (see Scheme 3) in the reaction product of FI or AI with sulfuric acid was clearly demonstrated by the absence of the UV spectral characteristics of the indolium cation (bands at 200, 234, 240 and 278 nm).¹⁹

The changes in the UV spectra of FI and AI in sulfuric acid (1.0 to 9.5 mol/dm³) show that in these cases protonation occurs on the carbonyl group (see Scheme 4).



Determination of the dissociation constants by the Hammett Acidity Function Method

If quantitative data are needed for comparison of very weak base strengths, it is convenient to use the Hammett Acidity Function Method (HAFM). Namely, for a weak base B in strongly acid media, K_a can be defined as the acid dissociation constant of the protonated form, BH^+ :

$$\text{B} + \text{H}^+ \rightleftharpoons \text{BH}^+ \quad (2)$$

$$K_a = a(\text{B})a(\text{H}^+)/a(\text{BH}^+) = \{c(\text{B})/c(\text{BH}^+)c(\text{H}^+)\} \{f(\text{B})f(\text{H}^+)/f(\text{BH}^+)\}$$

where a is the activity, c is the concentration and f is the activity coefficient. The logarithm form of Eq. (2) gives the thermodynamically correct equation:

$$\text{p}K_a = \log \{c(\text{BH}^+)/c(\text{B})\} - \log \{c(\text{H}^+)\} - \log \{f(\text{B})f(\text{H}^+)/f(\text{BH}^+)\} \quad (3)$$

Hammett and Deyrup¹³ postulated that an acidity function H_0 may be defined as an extension of the pH scale:

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

It has been shown that equations of the above form give acidity functions applicable only to closely related compounds (*e.g.*, H_A for amides,¹⁸ H_i for indoles,^{5,7} *etc.*).

The $\text{p}K_a$ values of the dissociation constants for the conjugate acids of MI, D-TrpH, FI, AI and ICAH were obtained using the values of $H_i(H_A)$ ^{5,18} and the ionization ratio ($\log I$) in the Hammett Eq. (5)

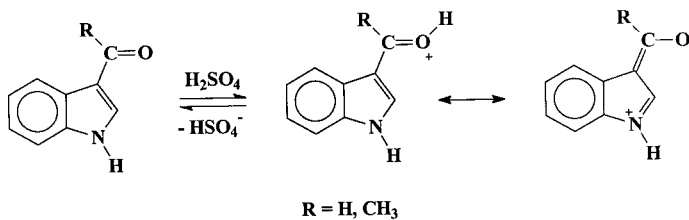
$$\text{p}K_a = H_i(H_A) + \log I \quad (5)$$

The method used for the calculation of the ionization ratio was same as the one presented in our previous paper.^{11,12} The values for pK_a for all the investigated compounds are shown in Table IV. It should be mentioned that the value for MI is in fair agreement with literature data.⁷

The value of the half protonation point (9.4 mol/dm^3) for tryptophan was reported by Podkovinska *et al.*¹ Substitution of this value into Eq. (6).

$$H_i = -0.69 c(\text{H}_2\text{SO}_4) + 0.227 \quad (r = 0.999) \quad (6)$$

(obtained by the least squares treatment of 21 data pairs H_i vs. $c(\text{H}_2\text{SO}_4)$), for the following condition $d(\log I)dH_i = 1$, a pK_a value of -6.2 is obtained. This value is in good agreement with the one obtained graphically (Table IV). On the other hand, the pK_a value is much smaller than the one calculated numerically (Table IV). The results for $d(\log I)H_i$ (denoted by m) of MI, D-TrpH and ICAH clearly show that H_i is a suitable acidity function for these indoles. The m values of MI, D-TrpH and ICAH do not deviate significantly from the values reported in the literature for other 3-alkyl or carboxyalkyl indoles. This behavior of the carbon bases MI, D-TrpH and ICAH strongly suggests that the positive charge is almost completely localized on the nitrogen atom. The hypothesis that FI, AI and ICAH should behave in a similar manner as amides in relation to acids was checked by treating our experimental results for three typical carbonylic indoles in sulfuric acid with the H_A function proposed by Yates *et al.*, for amides.¹⁸ The slopes of the plot $\log I$ against H_A are close to 1 (Table IV), except for ICAH. Such results seem to be sound evidence that FI and AI follow the H_A function to a good approximation. Our pK_a values for FI, AI and ICAH indicate that FI or AI are by about 6 pK_a units more basic than ICAH. The explanation for this difference may be offered in terms of resonance stabilization which produces much larger changes in basicity for FI or AI (see Scheme 5) than for ICAH.



Scheme 5.

Determination of the dissociation constants by Excess Acidity Method

The EAM is a method based on free energy relationships. It does not make use of any acidity functions, but gives pK_a values which refer to infinitely dilute water solutions as the standard state. The solvent parameter m^* obtained using this method are probably best interpreted in terms of solvation changes. The dissociation constant (pK_a) and solvent parameter (m^*) were obtained from Eq. (8).

$$\log I - \log \{c(\text{H}^+)\} = \log \{f(\text{B})f(\text{H}^+)/f(\text{BH}^+)\} + \text{p}K_{\text{a}} \quad (7)$$

$$\log I - \log \{c(\text{H}^+)\} = m^* X + \text{p}K_{\text{a}} \quad (8)$$

where X is the Excess Acidity Function.¹⁴

In this work, the X values were calculated in the range of 1.0 to 17.0 mol/dm³ using Eq. (9).

$$X = a_1(z - 1) + a_2(z^2 - 1) + a_3(z - 1) + a_4(z^4 - 1) + a_5(z^5 - 1) \quad (9)$$

where $z = \text{antilog}(w/100)$ and a_1, a_2, a_3, a_4, a_5 are polynomial coefficients.

The values of the weight fraction of sulfuric acid (%) were obtained directly from the acid concentration (in mol/dm³), using the published densities¹⁴ at 298 K.

The revised EAM $\text{p}K_{\text{a}}$ values for the investigated substances (Table IV), in most cases, differ from those obtained by the HAFM. The different $\text{p}K_{\text{a}}$ values result from limitations of the HAFM. The zeroth-order approximation²⁶ (activity coefficients for two bases are the same) is of importance when using the HAFM.

In addition, both methods give $\text{p}K_{\text{a}}$ values in reasonable agreement in the low acidity range (FI and AI). Deviations are observed for progressively weaker bases (MI, D-TrpH and ICAH). Also, the $\text{p}K_{\text{a}}$ value obtained by the EAM are smaller compared to those calculated by the HAFM (Table IV). Analysis of the $\text{p}K_{\text{a}}$ values of the investigated indoles (by the two methods) gives the following order of basicity:

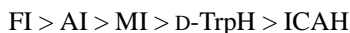


TABLE IV. $\text{p}K_{\text{a}}$ values (determined numerically and graphically) for all the studied indoles

Ions	Numerical $\text{p}K_{\text{a}}$	Graphically $\text{p}K_{\text{a}}(X)$	Graphically $\text{p}K_{\text{a}}(H_i)$	c_m	c_m^*
MIH ⁺	-4.6-0.2	-3.9-0.2 ^b -4.03	-4.011-0.2 ^a -4.55	-0.9 (-0.962)	1.3-0.2 (0.860) ^b 1.4
D-TrpH ₂ ⁺	-5.4-0.1	-4.2-0.3	-6.2-0.1	-1.1 (-0.971)	1.8-0.2 (9.968)
FIH ⁺	^d -1.7-0.1	-1.0-0.1	^d -2.2-0.1	^d -1.2 (-0.985)	1.2-0.1 (0.986)
AIH ⁺	^d -1.4-0.2	-1.3-0.1	^d -2.1-0.1	^d -1.4 (-0.996)	0.8-0.1 (0.997)
ICAH ⁺	-8.3-0.2 ^d -3.7-0.2	-6.8-0.3	-10.8-0.2 ^d -11.8-0.2	(-1.3 (-0.997) ^d -2.9 (-0.997)	1.1-0.05 (0.981)

^aRef. 7, ^bRef. 15 ^cThe number is parentheses in the correlation coefficient. ^dObtained using H_{A} function

This order is in good agreement with the one found by Andonovski *et al.*¹² in perchloric acid. The m^* values of MI, D-TrpH and ICAH do not deviate from the values reported in the literature.²⁷ The m^* values for these compounds correspond-

ing to the greater delocalization of the positive charge in the pyrrole ring. Further, the m^+ values of FI and AI deviate appreciably from typical values for carbon bases. On the other hand, the m^* values for FI are close to the values for oxygen bases, such as amides (>0.6).

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ИЗВОД

СТУДИЈА ПРОТОНАЦИЈЕ И ОДРЕЂИВАЊА КОНСТАНТЕ ДИСОЦИЈАЦИЈЕ
3-МЕТИЛ ИНДОЛА, D-ТРИПТОФАНА, ИНДОЛИЛ-3-КАРБАЛДЕХИДА,
ИНДОЛИЛ-3-МЕТИЛ КЕТОНА И ИНДОЛИЛ-2-КАРБОКСИЛНЕ КИСЕЛИНЕ У
СУМПОРНОЈ КИСЕЛИНИ ПОМОЋУ УЛТРАЉУБИЧАСТЕ СПЕКТРОФОТОМЕТРИЈЕ

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Проучавана је протнација индолил-3-карбалдехида, индолил-3-метил кетона, индолил-2-карбоксилне киселине, D-триптофана и 3-метил индола у сумпорној киселини UV-спектроскопијом у области између 400 и 190 nm. Израчунати су моларни апсорпциони коефицијенти помоћу вредности за апсорбације измерене на четири изабране таласне дужине. Резултати су искоришћени за израчунавање pK_a вредности за реакцију протонације. Тестиран је Хаметов постулат (нагиб на графику зависности $\log [c(BH^+)/c(B)]$ у односу на H би требало да буде једнак јединици). Константа дисоцијације и параметар растварања m^* су добијени применом такозване Excess Acidity методе. Дискутирана је позиција адираних протона у протонираним једињењима.

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