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UV Study of the Protonation of Indole and 3-Substituted Indoles in Perchloric Acid Media

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The protonation of indole, indolyl-3-acetic acid, indolyl-3-propionic acid and indolyl-3-butyric acid in perchloric acid media was studied by the methods of ultraviolet spectroscopy in the 320–190 nm region. The absorbance values were measured at several selected wavelengths and the molar absorptivity was calculated. From these values, using the Hammett's equation: $pK_a = H + \log[c(BH^+)/c(B)]$ where H is H_0 or H_i (*i.e.* Hammett's acidity function or its corrected value), the pK_a values for the reaction of protonation were obtained. The Hammett's postulate (the slopes of the plots $\log [c(BH^+)/c(B)]$ *vs.* H should be equal to 1) was tested. Also, the dissociation constants and the solvent parameter m were obtained by application of the Excess Acidity Method. The position of the additional protons in the protonated compounds was discussed.

INTRODUCTION

The indole derivatives are very weak bases. They accept a proton only in strong mineral acid media and give a cation. Hinman and Whiple[1] assumed that the protonation takes place at position 3. The positive charge is distributed over positions 1 and 2 (Scheme 1).

These assumptions were made on the basis of ultraviolet absorption spectra (UV) and were confirmed by proton-magnetic resonance measurements on a series of alkyl-indoles. Some evidence for 1-protonation was provided by the infrared spectra of solid salts of alkyl-indoles, which show the

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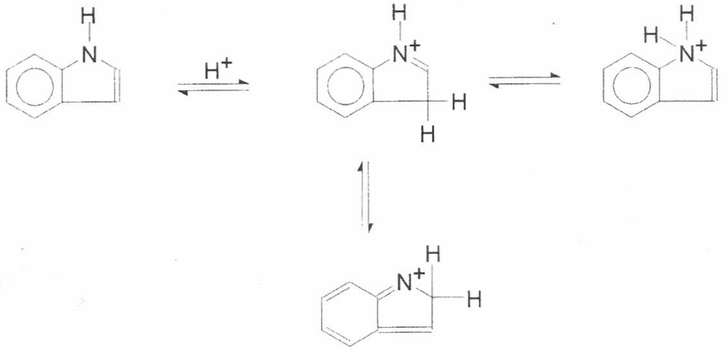


Scheme 1.

presence of 1 and/or 3-protonated species, depending on the indole type, the mineral acid and the method of salt isolation.

In an attempt to reveal the molecular structure of the indolic cation, the authors[1] compared the ultraviolet spectra of indole in strong mineral acid (H_2SO_4) with the UV spectra of compounds having a similar molecular structure. They concluded that the UV spectra of indole in strong mineral acid are similar to the UV spectra of solid salts of indolenine.

The dissociation constants of indole and five of its methyl derivatives have already been reported.[2] Since these results were based on the use of the H_0 acidity function, these numerical values differ from those obtained by Hinman and Lang.[3] Nevertheless, the order of appearance is identical in both sequences.

Due to the close structural similarity of the twenty-four indoles, the slopes of the plots of $\mathrm{d}(\log I)/\mathrm{d}\{c(H_2SO_4)\}$ (I is the ratio of the concentrations of protonated and deprotonated base forms and $\{c\}$ is the numerical value of the concentration) may be divided into three groups:

For the largest group, containing eighteen indoles, $\mathrm{d}(\log I)/\mathrm{d}\{c(H_2SO_4)\} = 0.700 \pm 0.03$. The other two groups (indoles unsubstituted in the hetero – ring) show $\mathrm{d}(\log I)/\ \mathrm{d}\{c(H_2SO_4)\} = 0.44 \pm 0.03$, while indoles which are 1,3 disubstituted have even higher slopes, *i.e.* $\mathrm{d}(\log I)/\mathrm{d}\{c(H_2SO_4)\} = 0.78 \pm 0.03$.[3] The indoles also deviate from H'_r, the acidity function that has been introduced for arylalkens to which the indoles bear some structural resemblance[3]: $H'_r = H_r - \log a(H_2O)$, where H_r is the acidity function for the complex dissociation of arylmethanols to the corresponding arylmethyl cations.[4]

The papers of Novotarska *et al.*[5,6] are of particular importance in the investigation of the proton-acceptor properties of indole compounds. These authors presented results for the proton-acceptor properties of the same indole compounds in sulfuric and perchloric acid media. In these investigations, they employed the methods of ultraviolet spectroscopy. They, first estimated the order of the protonation for the series of 3-substituted indoles in perchloric and sulfuric acid by the application of Hammett's acidity function and by graphical methods. In their subsequent study,[7] they extended their investigations over other similar indole compounds and concluded that the basicity decreases in the order:

gramine > triptamine > trypthophan > indol-3-butyric acid >
> indolyl-3-propionic acid > indolyl-3-acetic acid >
> 5-hydroxy-indolyl-3-acetic acid

Also, on the basis at the protonation properties, the authors divided these compounds into three classes:[7]

I. indolyl-3-ethanol, indolyl-3-butyric acid, indolyl-3-propionic acid, indolyl-3-acetic acid, trypthophan, tryptamine.
II. gramine
III. 5-hydroxy-indolyl-3-acetic acid.

The goal of the present study is to calculate the values of the dissociation constants for the conjugated acids of indole, indolyl-3-acetic acid, indolyl-3-propionic acid and indolyl-3-butyric acid in perchloric acid media using the Hammett Acidity Function Method (HAFM) and Excess Acidity Method (EAM). For these compounds, there is either a lack of numerical data in the literature or the reported values differ appreciably. In order to get the most probable values for the dissociation constants, the measurement of the UV absorbances was performed in the region of long and short wavelengths. The numerical and graphical calculations were done using the MATCHCAD computer program.

EXPERIMENTAL

The solutions of concentration 0.001 mol/dm^3 were prepared of indole and its derivatives in mixtures of water and ethanol (1.0 vol. %). Other more diluted solutions were prepared from these solutions by keeping the concentration of indole (or the derivative) constant and varying the concentration of perchloric acid (between 0.1 and 10.0 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.

The UV spectra of each solution were recorded between 320 nm and 190 nm on a Hewlett-Packard 8452A Diode Array Spectrophotometer. The absorbances were measured in 1 cm long quartz cells at eight analytical wavelength (Tables Ia and Ib). A solution of perchloric 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 ± 0.2 °C in a thermostated cell.

TABLE Ia

Absorbance (UV spectrum) and concentration data for indole

$c(\mathrm{HClO_4})$ mol dm^{-3}	A $\lambda = 196$ nm	A $\lambda = 204$ nm	A $\lambda = 210$ nm	A $\lambda = 216$ nm
1.0	0.8383	0.9662	1.1780	1.3400
2.0	0.7855	0.9405	1.1820	1.3660
4.0	0.7370	0.9426	1.0960	1.2200
5.0	0.4016	0.7007	0.8140	0.8771
5.5	0.4911	0.6944	0.7225	0.7182
6.0	0.3870	0.6285	0.5756	0.4953
6.5	0.4078	0.5859	0.4788	0.3566
7.0	0.2836	0.5067	0.3566	0.1812
7.5	0.3198	0.5120	0.3672	0.2167
8.0	0.3311	0.5794	0.4234	0.2468
8.5	0.2658	0.4809	0.3232	0.1566
9.0	0.3132	0.5445	0.3770	0.1950
9.5	0.2003	0.4671	0.3135	0.1357
10.0	0.2317	0.4560	0.3181	0.1515

TABLE Ib

Absorbance (UV spectrum) and concentration data for indole

$c(\mathrm{HClO_4})$ mol dm^{-3}	A $\lambda = 270$ nm	A $\lambda = 278$ nm	A $\lambda = 286$ nm	A $\lambda = 292$ nm
1.0	0.2857	0.2982	0.2462	0.1654
1.5	0.2533	0.2715	0.2214	0.1415
2.0	0.2579	0.2708	0.2186	0.1392
2.5	0.2809	0.2919	0.2371	0.1552
3.0	0.2470	0.2579	0.2069	0.1287
3.5	0.2849	0.2950	0.2448	0.1675
4.0	0.2827	0.2912	0.2308	0.1401
4.5	0.2415	0.2499	0.2007	0.1426
5.0	0.2376	0.2498	0.2032	0.1266
5.5	0.2503	0.2632	0.2158	0.1385
6.0	0.2020	0.2061	0.1553	0.0786
7.0	0.2222	0.2299	0.1879	0.1183
7.5	0.2569	0.2667	0.2298	0.1667
8.0	0.2266	0.2444	0.2256	0.1822
8.5	0.2064	0.2311	0.2268	0.2000
9.0	0.1677	0.1987	0.2035	0.1867
9.5	0.1700	0.2034	0.2127	0.2016
10.0	0.2064	0.2420	0.2526	0.2408

The values of the molar absorptivity of indole and 3-carboxyalkyl indoles, ε_{B}, were estimated in 1.0 mol/dm^3 $HClO_4$. The molar absorptivity of the protonated form of the investigated compounds, $\varepsilon_{\mathrm{BH}^+}$, was estimated at a high enough concentration of perchloric acid, so no further change occurred in ε after increasing the $c(HClO_4)$ to 10.0 mol dm^{-3}. The indole and 3-carboxyalkyl indoles were MERCK products. The physical properties of these compounds were in good agreement with the literature values. Solutions of perchloric acid were prepared by dilution of MERCK-ALKALOID reagent grade acid (70% by weight).

RESULTS AND DISCUSSION

The absorption spectra of indole and 3-carboxy alkyl derivatives in non-polar and polar solvents show four bands: ^1B_a, ^1B_b, ^1L_a and ^1L_b. Band ^1B_b has a somewhat greater intensity and more pronounced vibrational fine structure (or more resolved) components than ^1B_a. Bands ^1L_a and ^1L_b have lower intensity compared to the ^1B_a and ^1B_b. All bands in the UV spectrum may be assigned to π-π^* transitions in the indolic ring.

However, in perchloric acid media, changes are noted in the position and intensity of the ^1B_a, ^1B_b, ^1L_a and ^1L_b bands in UV spectra of indole or the 3-substituted indoles. By increasing the concentration of the mineral acid, the intensity of the ^1B_a and ^1B_b bands decreases, showing at the same time red shifts (Figure 1.), in agreement with the literature data.[8]

When these compounds are recorded in more concentrated solutions (*e.g.* 6.0 mol/dm^3, rather than in 1.0 mol/dm^3 $HClO_4$), pronounced changes occur.

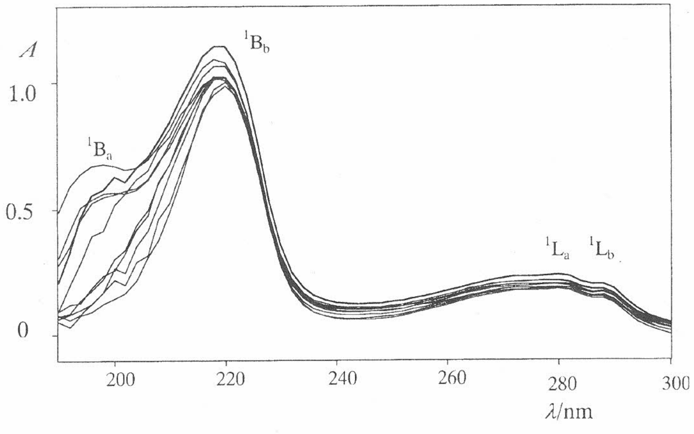


Figure 1. Ultraviolet absorption spectra of indolyl-3-acetic acid (c = 4.0 10^{-5} mol/dm^3) in solutions of different concentration of $HClO_4$ (top to bottom, at left-hand margin) 0.1; 0.2; 0.3; 0.4; 0.5; 0.6; 0.7; 0.8; 0.9 and 1.0 mol/dm^3).

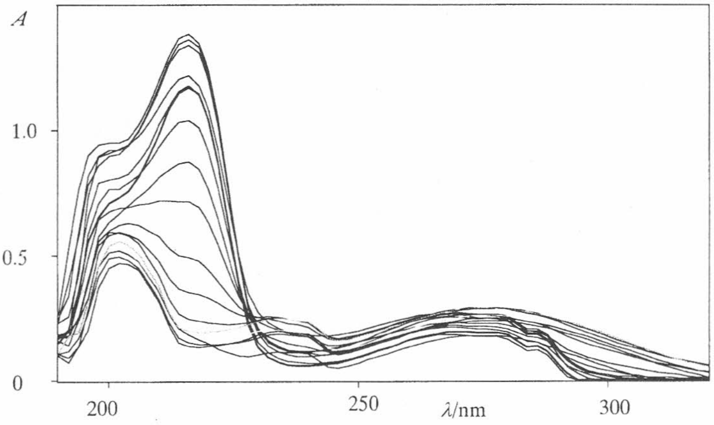


Figure 2. Ultraviolet absorption spectra of indolyl-3-acetic acid (c = 4.0 10^{-5} mol/dm^3) as function of perchloric acid concentration. Solvent (top to bottom, at position of λ = 220 nm) perchloric acid 1.0; 2.0; 3.0; 3.5; 4.0; 4.5; 5.0; 5.5; 6.0; 6.5; 7.0; 7.5; 8.0; 8.5; 9.0; 9.5 and 10.0 mol/dm^3).

For example, the ^1B_b band of indolyl-3-acetic acid (IAAH) in perchloric acid with a concentration of 9.0 mol/dm^3 disappears (Figure 2). The appearance of new bands at 204, 234 and about 238 nm, may also be noted in the spectra of this solution (Figure 2). In the long-wavelength region, ^1L_a and ^1L_b bands are shifted to even longer wavelengths and grow in intensity *e.g.* the band at about 270 nm is shifted to ~ 280 nm (Figure 2). The changes in the spectrum of IAAH shown in Figure 2 are typical of the 3-carboxy alkyl indoles.

The observed transitions of the UV spectra of IH_2^+, $IAAH_2^+$, $IPAH_2^+$ and $IBAH_2^+$ are shown in Table II. This Table, for purposes of comparison, also includes the literature data for the calculated and experimentaly found transitions in the UV spectrum of $IAAH_2^+$ in sulfuric acid.[9] The spectrum of the $IAAH_2^+$ ion in perchloric acid is not in very good agreement with the spectrum of $IAAH_2^+$ in sulfuric acid, probably due to various solvent effects.

The observed changes are beyond doubt a result of the protonation of the indolyl group in 3-substituted indoles and are in very good agreement with literature data.[1] That is, in the presence of higher concentrations of $HClO_4$ (above 6.0 mol/dm^3), the 3-carboxy-alkyl indoles are protonated. Effects of the medium on the spectra of the indole forms (B and BH^+), in the 250–190 nm region, appear to be less significant. This is confirmed by the existence of isobestic points in the 250–190 nm region. On the other hand, there is no isobestic point in the 320–250 nm region, probably due to the existence of three spectral forms (BH, BH^+, BH^+A^-) present, which absorb in this part of the spectrum, and/or the effect of the solvent ($HClO_4$ – H_2O). Lack of a

TABLE II

Experimental transitions in the UV spectra of IH_2^+, $IAAH_2^+$, $IPAH_2^+$ and $IBAH_2^+$

Ions transitions	IH_2^+	$IAAH_2^+$	$IAAH_2^{+*}$	$IPAH_2^+$	$IBAH_2^+$
			λ / nm		
^1L_b	276.0	288.0	295.5	290.0	276.0
^1L_a	----- 240.0(sh)	----- 242.0(sh)	255.0 240.0(sh)	----- 242.0(sh)	----- 242.0(sh)
^1B_b	232.0	234.0	231.0	234.0	232.0
^1B_a	204.0	202.0	-----	200.0	202.0

* [8] – F. Tomas-Vert, C. A. Ponce, M. R. Estrada, J. Silber, J. Singh, and J. Anunciatta, *J. Mol. Strcut* **246** (1991) 203.

well-defined isobestic point is sometimes attributed to solvent effects, which in this particular case most probably appear, due to the non-constant value of the molar absorptivity for the base and the conjugated acid.[10]

The plot of the absorbance (at λ = 216 nm) *vs.* H_i for indole gives a non-linear curve (*cf.* Figure 3), thus indicating a decrease of the concentration of the unprotonated form (in the region of –2.0–5.0 H_i). The curve shown in Figure 3 is typical of the other investigated substances, as well.

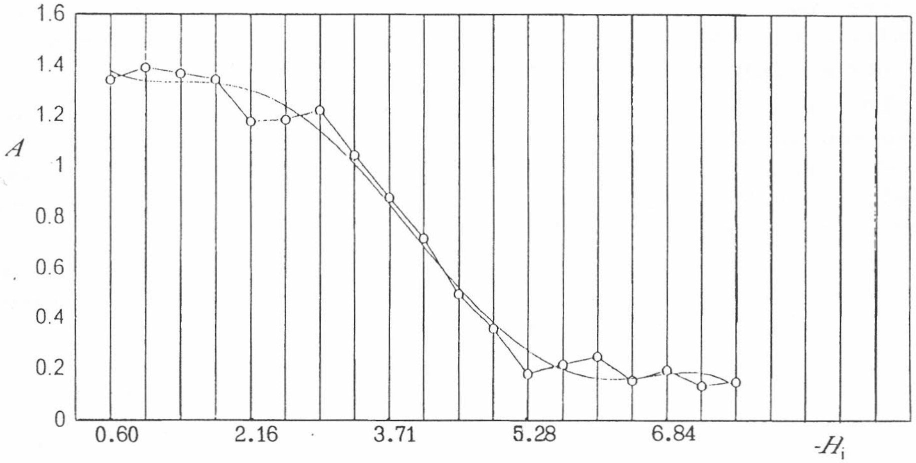


Figure 3. Effect of acidity function on absorbance at 216 nm of indole.

For quantitative characterization of the protonation reaction, Hammett's equation was used,[11] according to which the pK_a value of the dissociation constant for the conjugate acid is presented by Eq. (1).

$$pK_a = H_o + \log [c(BH^+)/c(B)] \tag{1}$$

In this equation, H_o is Hammett's function, $c(BH^+)$ and $c(B)$ are concentrations of the conjugated acid (BH^+) and free base (B), respectively. When a monoprotonation reaction takes place, the following condition (*cf.* Eq. (2)) has to be fulfilled:

$$d(\log I)/dH = 1 \tag{2}$$

Using the values for H_o and H_i (the functions of indoles in perchloric acid with a concentration up to 6.0 mol/dm^3 $HClO_4$,[3] the least squares treatment for 15 data pairs gave the following linear equation:

$$H_i = 1.419\ H_o - 0.519\ (r = 0.999) \tag{3}$$

The values for H_i were obtained by extrapolation of the equation in a concentration range of 6.0–10.0 mol/dm^3 in perchloric acid media. Since there are no literasture data for H_{indole}, the dissociation constant of indole in perchloric acid was calculated using H_i function.

In order to determine the ionization ratio $I\{[I = c(BH^+)/c(B)]\}$ in Hammett's Eq. (1), the absorbances were measured at eight analytical wavelengths: four in the region of short and four in the region of long wavelengths for each compound (Table Ia, Ib). The number of data points may be considered as large enough, so the estimated values of pK_a are expected to be reliable.

The calculations of pK_a were done using values for the H_o, H_i[3] and X[12] functions. The method used for the calculation of pK_a values was similar to the one presented in our previous papers.[13,14]

The values for pK_a for all investigated compounds calculated from the measured absorbances in the region of long and short wavelengths are shown in Table III, together with the mean values and standard deviations of pK_a. It should again be mentioned that these data are in fair agreement with literature data.[5–7]

According to the values for pK_a calculated from experimental data by the numerical method (the absorbances measured in the region of short wavelengths), the order of protonation is as follows:

indole > indolyl-3-butyric acid > indolyl-3-propionic acid >
> indolyl-3-acetic acid

Once again, this order is in good agreement with thew one found by Novotarska *et al.*[5–7]

It is obvious from Table III that the standard deviations in the pK_a values are much smaller than those calculated from the absorbances measured in the region of short wavelengths, thus indicating that these values are more accurate than those calculated from the absorbances in the long wavelenght region.

TABLE III

Numerically and graphically determined pK_a values for the four investigated indoles

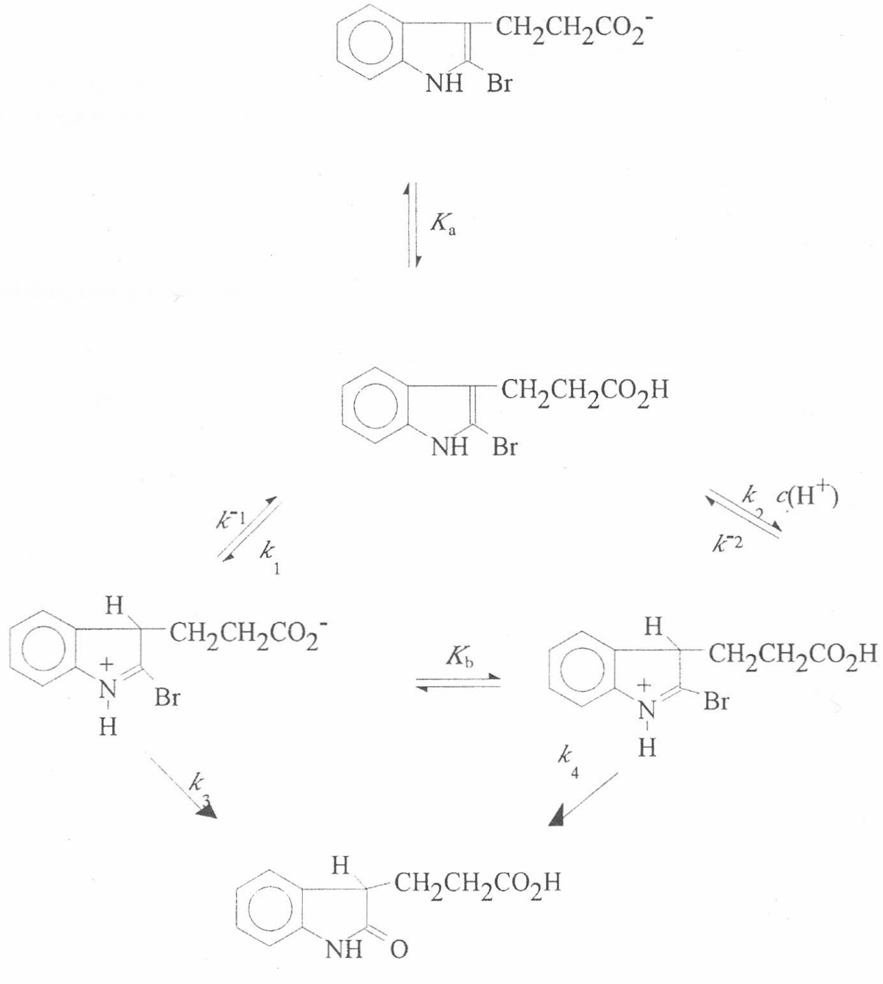
Long wavelengths				
Compounds	Indole	Indolyl-3-acetic acid	Indolyl-3-propionic acid	Indolyl-3-butyric acid
Range of acid concentration over which slopes were measured	4.0–6.5 mol dm^{-3}	6.0–8.5 mol dm^{-3}	6.0–8.5 mol dm^{-3}	6.0–9.0 mol dm^{-3}
$d(\log I)/d\{c\}$ $HClO_4$	0.71	0.77	0.69	0.50
$d(\log I)/dH_0^*$	–1.21	–1.06	–0.94	–0.85
$d(\log I)/dH_i^*$	–0.85	–0.75	–0.66	–0.61
m	1.24	0.89	0.93	0.71
pK_a(EAM)*	–2.80	–3.78	–3.83	–3.13
X(pK_a)**	–2.57 ± 0.18	–4.22 ± 0.13	–4.15 ± 0.13	–4.11 ± 0.11
X(pK_a)***	–4.13 ± 0.15	–6.37 ± 0.18	–6.22 ± 0.40	–6.28 ± 0.30
Short wavelengths				
$d(\log I)/d\{c\}$ $HClO_4$	0.91	0.74	0.75	0.54
$d(\log I)/dH_0^*$	–1.16	–1.10	–1.23	–1.19
$d(\log I)/dH_i^*$	–1.17	–0.95	–0.97	–0.69
m	1.60	1.02	1.10	0.60
pK_a(EAM)*	–3.60	–3.96	–3.95	–2.23
X(pK_a)**	–2.47 ± 0.12	–4.35 ± 0.11	–3.86 ± 0.20	–3.40 ± 0.15
X(pK_a)***	–4.03 ± 0.17	–6.52 ± 0.17	–5.94 ± 0.20	–5.57 ± 0.17

* Calcd. by least squares

** Calcd. by numerical method and H_o

*** Calcd. by numerical method and H_i

* Calcd. by graphical method and X



Scheme 2.

The present results on the protonation of different indoles clearly show that the slope slog I vs. H_o or H_i is very different from 1 (see Table III). The deviations are, most probably, a result of the different solvation of the bases and conjugated acids; alternatively, one may question the validity of the Hammett activity coefficient postulate. Therefore, the reported pK_a (H_o) and pK_a(H_i) may not represent the true thermodynamic pK_a, since no correlation exists between the ionization data and the acidity functions. Anyway, the above pK_a' values are very often considered as data of great practical significance (for example, a good correlation between the Hammett's σ_m constants of the substituents and pK_a' values has been found.[15]

Nowadays, it is well established that the acid – base behaviour of weak acids and bases in non-ideal aqueous media may be described by, at least, two parameters, which must reflect the internal and external stabilization of the acid – base conjugate pairs as a result of the molecular structure itself and the solvation process, respectively.[16] The approach based on the Excess Acidity Methods proved to be very useful for that matter. The revised EAM pK_a for the investigated substances (Table III), in most cases, differ from those obtained by HAFM. Thus, by comparison of the protonation parameters of the base, no clear relationship between pK_a amd m may be found. The m value of indole does not deviate significantly from the value reported in literature.[16] One, then, might be tempted to interpret this greater m value for indole as corresponding to greater delocalization of the positive charge in the pyrrole ring.[16]

This behaviour of the carbon bases, indolyl-3-acetic, indolyl-3-propionic and indolyl-3-butyric acids strongly suggests that the positive charge is almost completely localized on the nitrogen atom. The m values of indolyl-3-acetic acid and indolyl-3-propionic acid deviate appreciably from the typical values of carbon bases (usually between 1.7 and 2.2). On the other hand, they are close to the values for nitrogen bases such as anilines (~ 1.0).

It is known from literature data for the mechanism of hydrolysis of 2-haloindoles[17] that the protonation of indoles is the first step in this chemical reaction (see Scheme 2). For this reason, the negative pK_a might be very useful in the investigation of the kinetics and mechanism of hydrolysis in strong acid media.

CONCLUSION

Values for the dissociation constants were determined for conjugated acids of indole, indolyl-3-acetic acid, indolyl-3-propionic acid and indolyl-3-butyric acid in perchloric acid media (Table III) using the H_o, H_i and X functions. Values of absorbances in the regions of short and long wavelengths in the UV spectra were used for the pK_a calculations. Yet, the limits of the existing spectrophotometric techniques preclude experimental determination for both very low and very high values of log $[c(BH^+)/c(B)]$. The calculations were done using the MATHCAD computter program and there is good agreement between these results and the literature data.[5–7] Somewhat unexpectedly, more precise values were obtained from the absorbances measured in the short wavelength region (usually the long wavelength region is preferred by other authors.[5–7] Above 250 nm, a systematic increase in $c(BH^+)$ and $c(B)$ was found.[1] In this range, the spectra of the protonated indoles and the free base are nearly coincident (Figure 2), so errors are expected to be quite large (Table III). The relative order of the protonation of these compounds is in agreement with that found by Novotarska *et al.*[5–7] The values obtained from the H_i function are by about two pK_a units greater than those obtained by the H_o function.

Although it was originally proposed that the activity coefficient ratio $f(BH^+)/f(B)$ should have the same values for all single-charged indicators in a given concentration of acid, a number of important exceptions to this postulate have been found.[18,19] Many deviations from H_0 are known to exist, showing clearly that, within the limits, there are two acidity functions corresponding to two wide classes of bases: those with protonated carbon and those with protonated nitrogen or oxygen; however, a continuum of functions between these limiting cases is likely to be found in different protonation equilibria.

It should be noted that the above mentioned value of H_0 does not represent »the edge« of this continuum, as the acidity function for indole has an even smaller slope. In short, it is clear that the idea of a generally applicable indicator-based acidity function, as introduced originally, is only an idealization and, in that sense, an oversimplification. The values obtained from the Excess Acidity Method are very different from those obtained by the Hammett Acidity Function Method.

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SAŽETAK

Studij protoniranja indola i 3-supstituiranih indola u perklornoj kiselini UV-spektroskopijom

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Protoniranje indola, indolil-3-propionske kiseline i indolil-3-maslačne kiseline u perklornoj kiselini studirano je ultraljubičastom spektroskopijom u području 320–190 nm. Vrijednosti apsorbancije izmjerene su za nekoliko izabranih valnih duljina i izračunana je molarna apsorptivnost. Iz ovih vrijednosti dobivene su vrijednosti pKa za reakciju protoniranja indolil-3-octene kiseline primjenom Hammettove jednadžbe: $pK_a = H + \log[c(BH)^+)/c(B)]$, gdje H označava H_0 ili H_i (tj. Hammettovu funkciju kiselosti ili njenu korigiranu vrijednost). Provjeren je Hammettov postulat ($\log[c(BH^+)/c(B)]$ trebao bi biti linearna funkcija H, s nagibom jednakim 1). Također su, primjenom postupka u suvišku kiseline, dobivene disocijacijske konstante i parametar otapala m. Razmatran je smještaj dodatnih protona na molekulama protoniranih spojeva.