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Original scientific paper

UV STUDY OF THE PROTONATION OF INDOLE AND SOME 3-CARBOXYALKYL INDOLES IN SULFURIC ACID MEDIA

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The protonation of indole, indolyl-3-acetic acid, indolyl-3-propionic acid and indolyl-3-butyric acid in sulfuric acid was studied by ultraviolet (UV) spectroscopy in the 400–190 nm region. The position of the additional protons in the protonated compounds was discussed. The absorbance values were measured at several selected short wavelengths and the molar absorptivities were estimated. From these values, using Hammett's equation, the pK_a values for indole, indolyl-3-acetic acid, indolyl-3-propionic acid and indolyl-3-butyric acid: –3.6 (± 0.1); –5.6 (± 0.4); 5.3 (± 0.1) and 4.9 (± 0.3), were obtained, respectively. The pK_a values (and the solvent parameter m*) were estimated using the Excess Acidity Method as well.

Key words: indole; indole derivatives; protonation; dissociation constants; solvent parameter; Excess Acidity Method; UV spectroscopy

INTRODUCTION

The knowledge of the dissociation constants of weakly basic substrates such as indoles is of central importance in the studies of the reaction mechanisms, particularly of the reactions taking place in acidic media [1, 2]. For this reason, we deemed it useful to examine the ultraviolet spectra of indole (IH), indolyl-3-acetic acid (IAAH), indolyl-3-propionic acid (IPAH) and indolyl-3-butyric acid (IBAH) in sulfuric acid. We decided to complete the investigation by determining the pK_a values of the studied compounds using the Hammett Acidity Function Method (HAFM) and the Excess Acidity Method (EAM) and by calculating the order of their basicity. In order to get the most reliable values for the dissociation constants, the measurement of the UV absorbances was performed in the short wavelength region (230 –190 nm).

It should be noted that the basicity of the indoles has been examined by many authors [3–6] using ultraviolet (UV) spectroscopy, probably the most important results being those of Hinman *et al*. [3, 7, 8]. Using Hammett's method of overlapping indicator ratio plots [9] and introducing the H_i function (*i.e.* the acidity function for indoles), these authors defined the acidity of the sulfuric acid solutions by determining the pK_a values in a series of eighteen indole derivatives. A linear dependence was found between the H_i function and the Hammett's H_0 function. Tabulated values for the H_i function could be used for the determination of pK_a values of other indoles which are protonated in H_2SO_4 using the Hammett acidity function method (HAFM). It was found that the pK_a values are well correlated with the substituent constants. It should be noted that the examined compounds proved to be unstable in sulfuric acid solutions, as evidenced by the time-dependent changes in their UV spectra. To circumvent these difficulties, time resolved absorbance spectra were recorded at λ = 222 nm and the absorbance values for t = 0 were obtained by linear extrapolation [7].

Cohen *et al.* [10] found that the pK_a values for eleven indole derivatives substituted with alkyl substituents in positions 2 or 3 obtained by Hinman *et al*. [7] can be satisfactorily reproduced by a simple linear equation relating the pK_a values and a complex theoretical parameter $\Sigma\sigma$ (eq.1), introduced in the following way (cf. eq. 2):

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$$pK_a = -8.64\ \Sigma\sigma - 2.80 \quad (1)$$

$$\Sigma\sigma = \sigma_p^+(2) + 0.60\ [\sigma_m^+(3) + 0.08\ D_s - 0.084] \quad (2)$$

where σ_p^+ and σ_m^+ are the electrophilic substituent constants for the substituents at positions 2 and 3 and D_s is the double bond stabilization parameter for 3-substitution [10].

Thomas-Vert *et al*. [11] presented the results of semiempirical molecular-orbital calculations (MINDO/3) for protonated indolyl-3-acetic acid ($IAAH_2^+$) in sulfuric acid and found good agreement between the theoretical values and those found experimentally. Using the graphical method [12] they determined the pK_a values, but present two values (–4.3 and –6.4) for pK_a. The authors discussed problems concerning the complexity of the spectra of the indolyl-3-acetic acid in sulfuric acid, the absence of isobestic points, and the possibility for existence of *diprotonated* forms at higher sulfuric acid concentration. Their conclusion was that the protonation in IAAH takes place on the indolyl group and carboxylic group. According to this investigation, the pK_a value of –4.3 probably corresponds to protonation of the indolyl group (the value for 3-methyl indole is –4.5), while the one at –6.4 comes from the protonation of the carboxylic group (the characteristic values for carboxylic acids are in the range –6 to –8). Unfortunately, no data needed for the calculation/determination of these constants were given in the paper [11].

Considering all facts mentioned above, it seemed worthwhile to undertake this study and to reinvestigate, partly, the systems investigated previously. A diode array spectrophotometer (which is much faster than conventional instruments, the scan time per full spectrum being about 0.1 s) was used in the course of the study so that there was no need to use extrapolation procedures.

EXPERIMENTAL

The solutions were prepared from reagent grade Merck indole, indolyl-3-acetic acid, indolyl-3-propionic acid and indolyl-3-butyric acid in the concentration range from 10^{-2} to 10^{-3} mol dm^{-3} in aqueous ethanol (10.0 % by volume). From these solutions, more diluted solutions were prepared, keeping the concentration of indole (or its derivative) constant (2.0 10^{-5} mol dm^{-3}) and varying the concentration of sulfuric acid (between 1.0 and 12.0 mol dm^{-3}). The degree of dilution was chosen so that the absorbance would have values between 0.1 and 1.0, at the studied wavelengths.

Sulfuric acid solutions were prepared from 96 % (by weight) reagent grade sulfuric acid (Merck–Alkaloid – Skopje) by dilution with distilled water. All solutions were standardized against appropriate solutions of bases. The UV spectra were recorded on a Hewlett-Packard 8452A Diode Array Spectrophotometer, between 190 and 400 nm. The absorbances were measured in an 1 cm quartz cells at selected wavelength (see Table 2). A sulfuric acid solution (with the same concentration as in the investigated solutions) was used as a blank.

In order to check the validity of the Beer's law, measurements were carried out at different concentrations of the indole derivative and the mineral acid. The measurements were performed 1 – 1.5 min after preparing the solutions, at 27 ± 0.2 °C in a termostated cell. Plots of log I – log $\{c(H_2SO_4)\}$ *vs*. the excess acidity function X [13], were obtained by a linear least-squares treatment. The braces denote numerical value of the corresponding quantity (in the present case, the numerical value of the concentration) and X is the difference between the observed acidity and the one which the system would have if it were ideal.The numerical and graphical calculations were performed using the MATHCAD computer package.

RESULTS AND DISCUSSION

1. *UV spectra of the investigated compounds in sulfuric acid*

The absorption spectra of indole and 3-carboxy alkyl derivatives in non-polar and polar solvents consist [14, 15] of four bands: ^1B_a, ^1B_b, ^1L_a and ^1L_b which are due to $\pi \rightarrow \pi^*$ transitions. The ^1B_b band has somewhat greater intensity and more pronounced (or better resolved) vibrational fine structure than ^1B_a, whereas the ^1L_a and ^1L_b bands have lower intensity than both ^1B_a and ^1B_b. The band at 195 nm in the spectrum of IAAH has been assigned to $\pi \rightarrow \pi^*$ transitions from the carboxylic group [14] in line with the similar assignment for the 106.5 nm band in the spectrum of acetic acid [16]. The bands from the carboxyalkyl groups in 3-

substituted carboxyalkyl indoles are apparently overlapped with the bands resulting from $\pi \rightarrow \pi^*$ transitions which are characteristic for the indole chromophore. Due to their relatively weak intensity, they are not expected to be an obstacle for following the protonation reaction of the indolyl group.

The UV spectra of indole (IH) in sulfuric acid with concentration ranging from 1.0 to 10.0 mol dm^{-3} are shown in Fig. 1, and those of IAAH are given in Fig. 2.

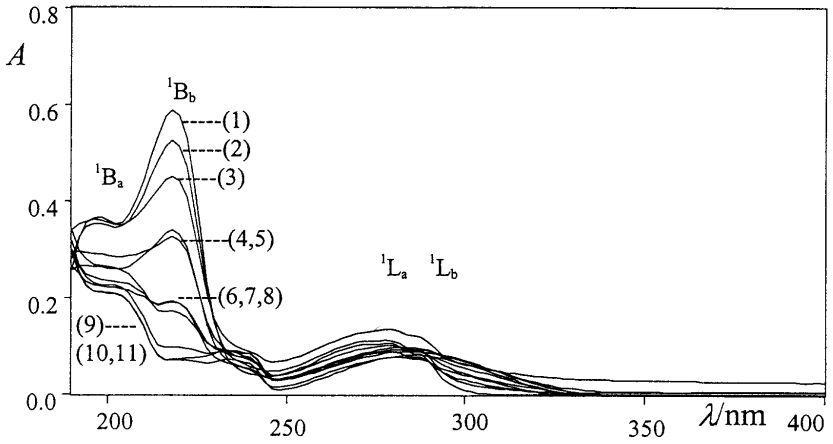


Fig. 1. Ultraviolet absorption spectra of indole (c = 2.0 10^{-5} mol dm^{-3}) as a function of sulfuric acid concentration. Solvent (top to bottom at position of λ = 216 nm) sulfuric acid 2.0 (1); 2.5 (2); 3.0 (3); 4.5 (4); 5.0 (5); 5.5 (6); 6.0 (7); 6.5 (8); 7.00 (9); 7.5 (10) and 8.0 (11) mol dm^{-3}

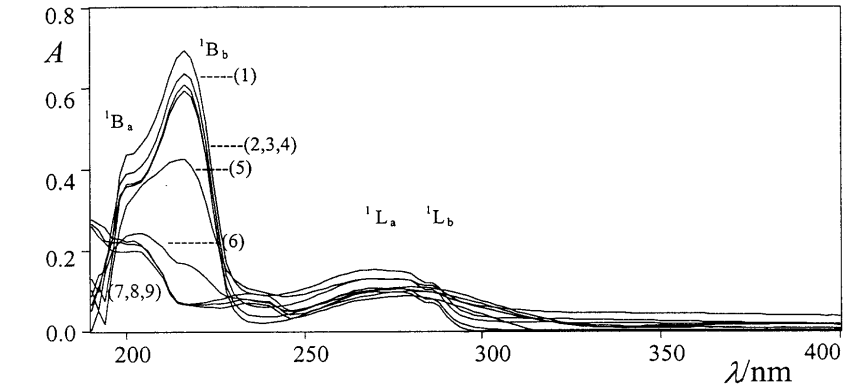
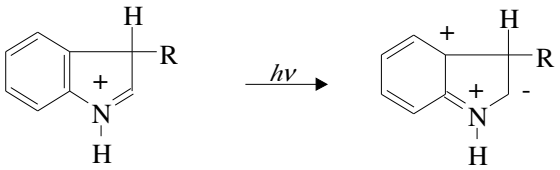


Fig. 2. Ultraviolet absorption spectra of indolyl-3-acetic acid (c = 2.0 10^{-5} mol dm^{-3}) as a function of sulfuric acid concentration. Solvent (top to bottom at position of λ = 220 nm) sulfuric acid 7.8 (1); 8.1 (2); 8.4 (3); 8.7 (4); 9.0 (5); 9.3 (6); 9.6 (7); 9.9 (8) and 10.2 (9) mol dm^{-3}

When H_2SO_4 concentration is 10.0 mol dm^{-3}, bands with maxima at 202, 234 and 280 nm (^1B_a, ^1B_b and ^1L_b, respectively) exist in the UV spectrum of indole (Fig. 1). The corresponding bands in the spectra of the substituted indole compounds may be detected at similar wavelength (at 200, 234, 240 and 280 nm in the spectrum of indolyl-3-acetic acid; at 196, 238, 240 and 292 nm in the case of

indolyl 3-propionic acid and at 200, 236, 240 and 288 nm in indolyl-3-butyric acid) but become clearly visible at a slightly higher concentration of sulfuric acid (12.00 mol dm^{-3}). As can be seen in the UV spectra of the studied indole compounds (Fig. 1 and 2)[1], the increase of the solution acidity causes bathochromic shifts of some bands and hypsochromic shifts of other ones, a fact already noticed by other authors [4–7,17].

The bands at 280, 280, 292 and 288 nm in the spectra of IH_2^+, $IAAH_2^+$, $IPAH_2^+$ and $IBAH_2^+$ ions respectively are due to the intramolecular charge-transfer transitions from the highest occupied orbital (HOMO or, according to the proposal of Nagakura and Tanaka [16], H_B) of the phenylene ring which acts as an electron donor to the lowest unoccupied orbital (LUMO or V_S) of the other part of the ion (the iminium group) which serves as an electron acceptor. These transitions are denoted HOMO → LUMO or $H_B \rightarrow V_S$. The ultraviolet absorption corresponding to the intramolecular charge-transfer transition may be represented by the following scheme:



Scheme 1

On the other hand, the bands at short wavelengths (about 200, 234 and 240 nm for the four studied compounds, respectively) are probably due to transitions within the phenylene ring.

The experimentally observed transitions in the UV spectra of IH_2^+; $IAAH_2^+$, $IPAH_2^+$ and $IBAH_2^+$ are shown in Table 1 (for comparison, the literature data for the calculated transitions in the UV spectrum of $IAAH_2^+$ [11] are also included). It should be noted that there is a difference in the position of the ^1L_b band between our spectrum and that presented by Vert *et al*. [11], probably due to various solvent effects. On the other hand, there is a remarkable disagreement between the calculated UV spectrum of $IAAH_2^+$ ion and the spectra of IH_2^+; $IAAH_2^+$, $IPAH_2^+$ and $IBAH_2^+$ (particularly around 250 nm; see Table I).

Table I

Experimental transitions in the UV spectra of the investigated compounds

ions	IH_2^+	$IAAH_2^+$	$IPAH_2^+$	$IBAH_2^+$	$IAAH_2^{+a}$
transitions			λ/nm		
^1L_b	280	280	292	288	295.5
^1L_a					255.0
		240(sh)	240(sh)	240	240
^1B_b	234	234	238	236	231
^1B_a	202	200	196	200	——

[a]Reference 11.

Variations in the H_2SO_4 concentration from 14.5 to 17.0 mol dm^{-3} had no significant effect upon the spectra of $IPAH_2^+$ (Fig. 3) but the ^1L_b band of $IAAH_2^+$ ion was bathochromically shifted to 308 nm (Fig. 4), the changes in the latter case being probably due to a new prototropic equilibrium which has been established. A band around 300 nm is reported [3–5] in the UV spectra of some 3-C protonated indoles (gramine, tryptamine) as well. Since the position and the intensity of the ^1L_b band in their UV spectra are strongly dependent on the concentration of the mineral acid (15.0 – 18.0 mol dm^{-3}) it is unlikely that they result from the protonation of carboxylic group.

The position and intensity of the ^1L_b band in our UV spectra of $IAAH_2^+$, $IPAH_2^+$ and $IBAH_2^+$ exhibit a very strong dependence upon the concentration of the mineral acid (14.5 – 17.0 mol dm^{-3}) which indicates that the protonation does not involve the carboxylic group. It is important to note that if this is true, the changes should not be used in the calculation of the second pK_a value (the corresponding equilibrium is a result of the protonation of the carboxylic oxygen atom).

The plot of the absorbance (measured at λ = 220 nm) *vs*. the H_i acidity function of H_2SO_4 for IAAH resulted in a roughly sigmoidal curve (cf. Fig. 5)[2] which indicates a decrease in the concentration of the unprotonated form in the range of $H_i(H_2SO_4)$ acidity function from –3.5 to –7.5. Analogous changes in the ultraviolet spectra were noted during the investigation of the protonation reaction of these compounds in perchloric acid [17].

[1]In Fig. 2 the changes in the spectrum of IAAH are shown. The changes observed in the case of indolyl-3-propionic acid and indolyl-3-butyric acid are similar.

[2] The curve shown in Fig. 5 is characteristic for the rest of the investigated substances as well.

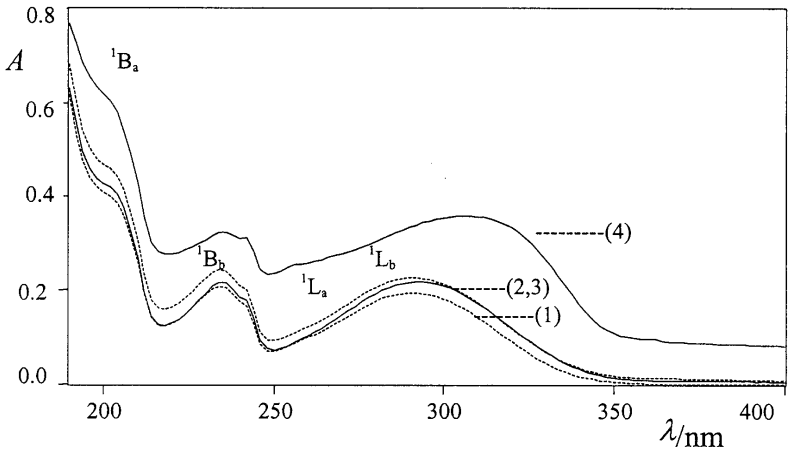


Fig 3. Ultraviolet absorption spectra of indolyl-3-acetic acid (c = 4.0 10^{-5} mol dm^{-3}) as function of sulfuric acid concentration. Solvent (bottom to top at position of λ = 290 nm) sulfuric acid 14.5 (1); 15.0 (2); 15.5 (3) and 16.5 (4) mol dm^{-3}

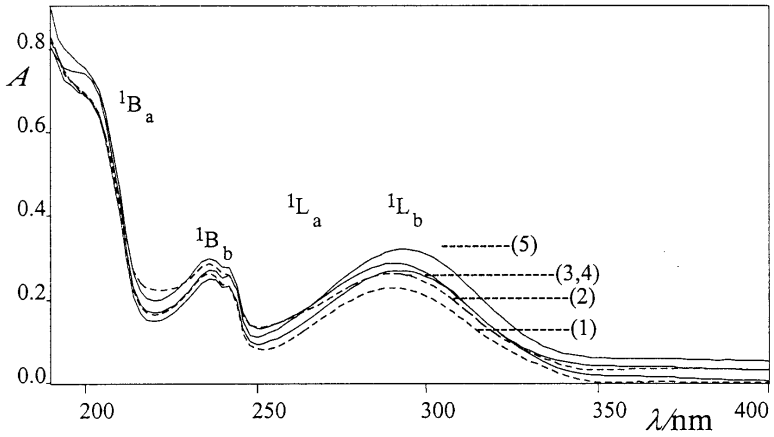


Fig. 4. Ultraviolet absorption spectra of indolyl-3-propionic acid (c = 4.0 10^{-5} mol dm^{-3}) as a function of sulfuric acid concentration. Solvent (bottom to top at position of λ = 290 nm) sulfuric acid 14.5 (1); 15.0 (2); 15.5 (3); 16.5 (4) and 17.0 (5) mol dm^{-3}

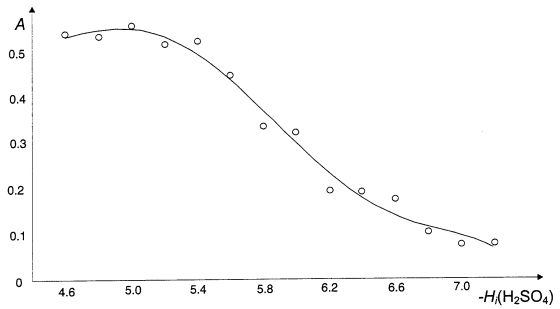
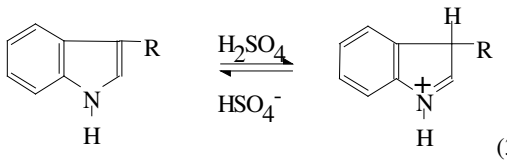


Fig. 5. Dependence of the indolic acidity function, H_i, acid on the absorbance at 220 nm for indolyl-3-acetic acid in sulfuric acid

Thus it may be assumed that the probability for the existence of different sites of protonation in unsubstituted and alkyl substituted 3-carboxylic indoles is very low, that the protonation of the indolic 3-carbon is the only reaction taking place (Eq. 3).



(3)

R = H; CH_2COOH; $(CH_2)_2COOH$; $(CH_2)_3$(COOH

In other words, carbonium ions derivatives are not formed and, under the described conditions, IH, IAAH, IPAH and IBAH could not be sulfonated.

2. *Determination of the dissociation constants*

The dissociation constants for the investigated compounds in sulfuric acid solutions were calculated from the absorbance values measured at short wavelengths. In an attempt to obtain more reliable pK_a values, the absorbances were measured at four wavelengths. The values of the molar absorptivities, ε_e(B), of IH, IAAH, IPAH and IBAH in 3.0, 5.5, 5.5 and 5.0 mol dm^{-3} H_2SO_4, respectively, were estimated and their logarithms are given in Table II. The molar absorptivity of the protonated form of the investigated compound, $\varepsilon(BH^+)$, was obtained from solutions in which the concentration of sulfuric acid was so high that no further changes occurred in ε with further concentration increase (the values are 7.5, 13.5, 13.5 and 11.0 mol dm^{-3}, respectively).

Table II

Molar absorptivity (log ε /mol^{-1}dm^{3}cm^{-1}) of the indoles in sulfuric acid solutions and wavelengths (λ/nm) used for dissociation calculations

cmpds	$c(H_2SO_4)$ /mol dm^{-3}	λ /nm and log ε /mol^{-1}dm^{3}cm^{-1}			
IH	3.0	194 (3.78)	212 (4.39)	216 (4.43)	218 (4.42)
–	7.5	– (4.05)	– (3.90)	– (3.82)	– (3.81)
IAAH	5.5	204 (4.39)	208 (4.45)	212 (4.53)	216 (4.60)
–	13.5	– (4.30)	– (4.21)	– (3.97)	– (3.80)
IPAH	5.5	206 (4.40)	210 (4.46)	214 (4.53)	220 (4.59)
–	13.5	– (4.08)	– (3.90)	– (3.52)	– (3.51)
IBAH	5.0	210 (4.80)	214 (4.27)	218 (4.35)	222 (4.38)
	11.0	– (3.83)	– (3.55)	– (3.46)	– (3.48)

Using the equation

$$\log I - \log \{c(H^+)\} = m^* X + pK_a \qquad (4)$$

where $I = c(BH^+)/c(B)$ is the protonation ratio, m^* is the solvent parameter and can be interpreted as a measure for the relative localization of the positive charge of the nitrogen atom, and X is Excess Acidity Function. The pK_a values were calculated using all available protonation ratio values. The m^* values obtained by application of EAM for these indole derivatives (between 1.7 and 2.2) are typical for values of carbon bases [13].

Using the values for log I and the H_i function and employing the Hammett's equation, the dissociation constants of 3-substituted indole compounds were determined. The same method has already been successfully applied for determination of pK_a values for the investigated compounds in perchloric acid media [17] and for other systems as well [18, 19].

The average pK_a values obtained by HAFM (a numerical method) and EAM (a graphical method) are listed in Table III together with the values for the solvent parameter m^*. The average standard deviation for the numerical values of pK_a was 0.2.

Table III

pK_a values (determined numerically and graphically) for all studied indoles

ions	numerically –pK_a (HAFM)	graphically –pK_a (EAM)	graphically –pK_a (HAFM)	m^{*e}
IH_2^+	3.6 ± 0.1; 4.0[d]	3.4 ± 0.2; 3.6[d]	3.5[a]	2.5± 0.1 (0.981)
$IAAH_2^+$	5.6 ± 0.4; 6.5[d]	6.8 ± 0.4 3.9[d]	6.3[a]; 6.1[b]; 6.4[c] and 4.5[c]	2.0 ± 0.1 (0.989)
$IPAH_2^+$	5.3 ± 0.1; 5.9[d]	5.9 ± 0.3; 3.9[d]	——	1.8 ± 0.1 (0.996)
$IBAH_2^+$	4.9 ± 0.3; 5.6[d]	5.8 ± 0.5; 2.2[d]	——	1.9 ± 0.2 (0.988)

[a] Reference 7. [b] Reference 5. [c] Reference 11. [d] Reference 17. [e] The number in parentheses is the correlation coefficient

The obtained pK_a values for IH_2^+ and $IAAH_2^+$ are in agreement with the Hinman's values. The value for $IAAH_2^+$ is, on the other hand, is different from that obtained by Tomas-Vert *et al.* [11] who used the acidity function (H_i) estimated from the absorbance values at only two wavelengths (260 and 300 nm). We believe that the value reported in the present paper is more reasonable and it is also closer to the values for pK_a($IAAH_2^+$) obtained by Hinman (see Table 3). It should be noted that the pK_a values for all compounds are lower than those obtained in perchloric acid [17]. The observed dif-

ferences in the pKa values determined in $HClO_4$ and H_2SO_4, respectively, are probably result of the different values of the indolic acidity function $H_i(H_2SO_4)$ or $H_i(HClO_4)$.

On the basis of the obtained results, the order of basicity of the investigated compounds in sulfuric acid may be given as follows:

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

The above order is in agreement with the data obtained by Novotarska *et al*. [4–6]. It is necessary to mention that these authors determined the pK_a values applying the same method as that used by Hinman [7], but with absorbance values measured in the region of *long* wavelengths (300 nm).

The large difference (approximately one pK_a unit) between the pK_a values for indolyl-3-acetic acid, on the one hand, and 3-methyl indole [7], on the other, is worth mentioning. The difference is quite pronounced, although both values were obtained by application of the same method. Apparently, the electrons within the indole chromophore are strongly polarized by those of the carboxylic group, and it is this polarization which makes indolyl-3-acetic acid less basic than 3-methyl indole.

The explanation for the effects shown by the alkyl and carboxyalkyl substituents on the basicity is fully confirmed by the notably good correlation of the experimentally determined pK_a values and the substituent constant values [10].

The stabilization of the cation which is due to a stronger inductive effect of the $-(CH_2)_2COOH$ and $-(CH_2)_3COOH$ groups compared with the one in $-CH_2COOH$, as well as the distance of the carboxylic group from the reaction center, increases the basicity which becomes closer to that of 3-methyl indole.

The large differences between the pK_a values for 3-carboxyalkyl substituted indoles (obtained in the present study) and those for 2-alkyl substituted derivatives, support Hinman's conclusions that selective potentiometric determination of 2-alkyl and 3-alkyl substituted indoles in mixture and 2-alkyl indole with 3-carboxylic alkyl indoles in mixture is possible.

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Р е з и м е

ПРОТОНИРАЊЕ НА ИНДОЛ И НЕКОИ НЕГОВИ ДЕРИВАТИ ВО СУЛФУРНА КИСЕЛИНА СО ПРИМЕНА НА УВ СПЕКТРОСКОПИЈА

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Клучни зборови: индол; индолови деривати; протонирање; константи на дисоцијација; солватационен параметар; метод на зголемена киселост; УВ спектроскопија

Испитано е протонирањето на индол, индолил-3-оцетната киселина, индолил-3-пропионската киселина и индолил-3-бутерната киселина во сулфурна киселина со примена на методите на ултравиолетова спектроскопија (УВ), во подрачјето на бранови должини од 400 до 190 nm. Дискутирана е и положбата на адираните протони кај протонираните соединенија. Вредностите на апсорбанцата се мерени на неколку селектирани бранови должини и од нив се определени моларните апсорпциони коефициенти. Од овие вредности, со примена на Hammett-овата равенка, пресметани се pK_a-вредностите за индол, индолил-3-оцетната киселина, индолил-3-пропионската киселина и индолил-3-бутерната киселина и тие се: –3,6(± 0,1); –5,6(± 0,4); 5,3(± 0,1) и 4,9(± 0,3), соодветно. Со примена на методот на зголемена киселост се определени pK_a-вредностите и солватациониот параметар m^*.