A STUDY OF THE BASICITY OF SOME HYDROXYBENZOIC ACIDS BY UV-SPECTROPHOTOMETRY

Marina GREBENKOVA and Ülo HALDNA

Eesti Teaduste Akadeemia Keemia Instituut (Institute of Chemistry, Estonian Academy of Sciences), Akadeemia tee 15, EE-0026 Tallinn, Eesti (Estonia)

Abstract. The basicity of three hydroxybenzoic acids, 2,5-dihydroxy-, 3,5-dihydroxy- and 3,4,5-trihydroxy-, was studied by the respective UV-absorption spectra measurements in aqueous sulfuric acid solutions (0—96% H_2SO_4, w/w). The spectra were obtained for a wide spectral range of 52000—28000 cm^{-1}, where two or three absorption bands were found to be present. A combination of the Cox-Yates excess acidity method, the curve fitting procedure and the Davis-Geissman method for shifting bands was applied to estimating the values of the basicity constant pK_{BH^+} and solvation parameter m^*. The following pK_{BH^+} and m^* values were obtained for the bases studied: 2,5-dihydroxybenzoic acid: $pK_{BH^+} = -5.67$, $m^* = 0.72$; 3,5-dihydroxybenzoic acid: $pK_{BH^+} = -7.08$, $m^* = 0.81$; and 3,4,5-trihydroxybenzoic acid: $pK_{BH^+} = -5.49$, $m^* = 0.69$.

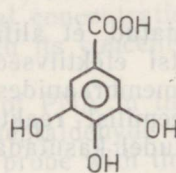**Key words:** hydroxybenzoic acids, protonation, UV-spectrophotometry.

In this work the basicity of three hydroxybenzoic acids (HBA): 2,5-dihydroxy- (I), 3,5-dihydroxy- (II) and 3,4,5-trihydroxybenzoic (III), was
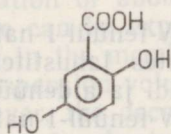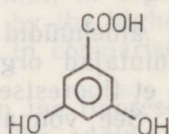
studied because (i) there is very little quantitative information [1–4] on the basicity of organic compounds containing a carboxyl and two or more hydroxyl groups in the molecule; (ii) the protonation process of these organic bases can be investigated by UV-absorption spectrophotometry.

In aqueous sulfuric acid the parent compound, benzoic acid, protonates on its carbonyl group [1, 2, 5]. This conclusion has been drawn from substituent effects [1, 5] as well as from some spectroscopic evidence [6–8]. We have not found any information about the protonation site of the benzoic acid obtained by NMR-spectroscopy.

EXPERIMENTAL

3,5-Dihydroxybenzoic acid (Merck) and 2,5-dihydroxy- and 3,4,5-tri-hydroxybenzoic acids obtained from Swedish National Food Administration were used without further purification. All the melting points of the above acids were found to be close to those given in the literature.

The preparation of sulfuric acid (chemically pure grade) solutions and the determination of their concentrations were carried out as described before [9].

The spectra of the HBA solutions were recorded on a SPECORD M40 spectrophotometer (Carl Zeiss Jena) at room temperature ($20 \pm 1 \, °C$) in quartz cells with path lengths of 2 and 10 mm. The concentrations of HBA were approximately $2 \cdot 10^{-4}$ M.

The methodology of the recovery experiments of the substances studied in the strongest sulfuric acid has been bescribed in [9]. The bases studied in this work (I, II and III) showed no noticeably irreversible reactions such as sulfonation during 15 minutes after the preparation of the solution.

CALCULATIONS

The UV-absorption spectra of I, II and III measured are presented in Figs. 1, 2 and 3, respectively. These spectra were divided into three regions in which the pK_{BH^+} and m^* values were calculated separately: region A ($52000{-}43000$ cm^{-1}), region B ($43000{-}36000$ cm^{-1}) and region C ($36000{-}28000$ cm^{-1}).

It should be noted that for III regions B and C were not separated: in the spectra of the 3,4,5-trihydroxybenzoic acid in the region $28000{-}44000$ cm^{-1} only one, but more intensive and wider, band was obtained (Fig. 3).

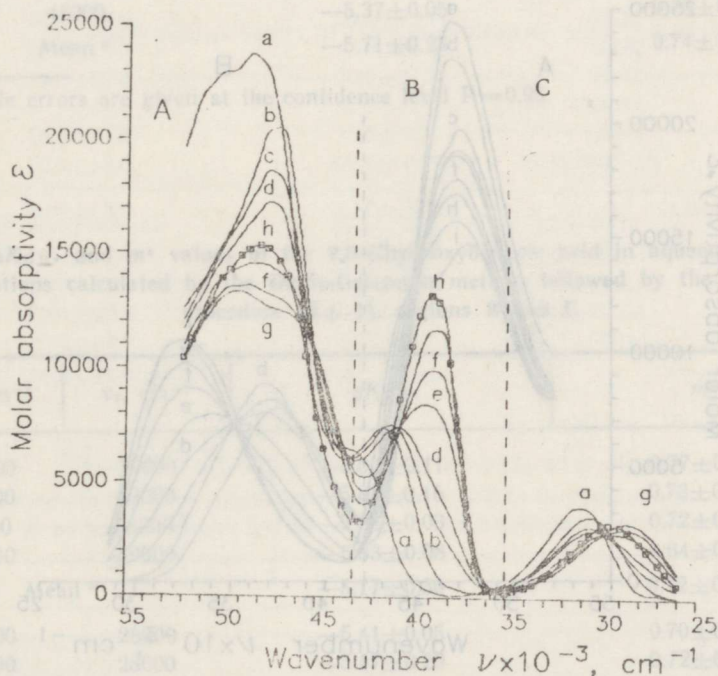Fig. 1. UV-absorption spectra of the 2,5-dihydroxybenzoic acid in aqueous sulfuric acid solutions. Sulfuric acid concentrations: a — 0, b — 68.9, c — 76.1, d — 78.4, e — 82.2, f — 84.5, g — 87.9, and h — 95.3%.

Fig. 2. UV-absorption spectra of the 3,5-dihydroxybenzoic acid in aqueous sulfuric acid solutions. Sulfuric acid concentrations: a — 0, b — 58.7, c — 78.9, d — 83.5, e — 85.8, f — 88.6, g — 90.7, and h — 95.2%.
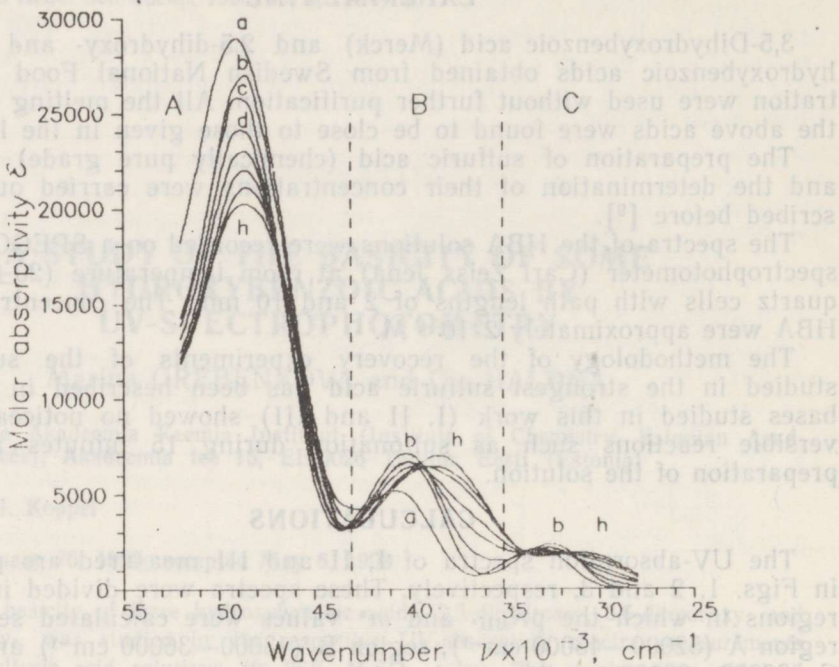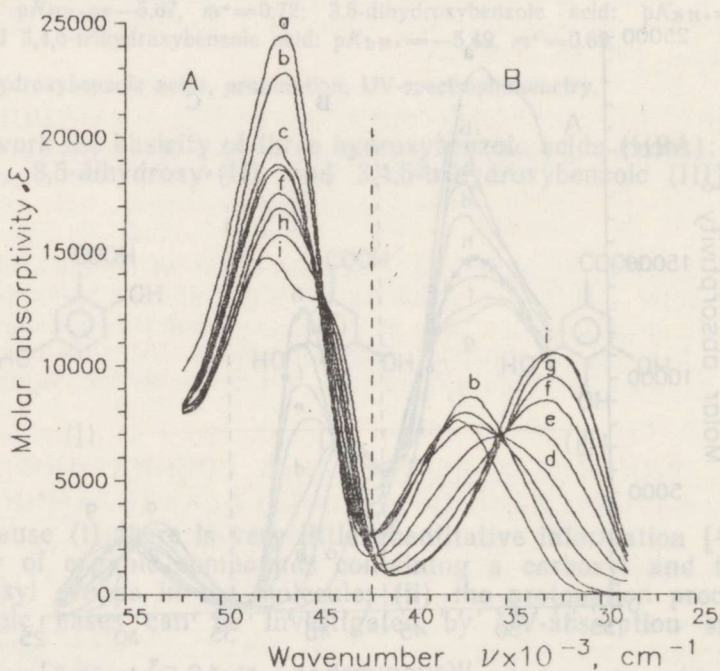

Fig. 3. UV-absorption spectra of the 3,4,5-trihydroxybenzoic acid in aqueous sulfuric acid solutions. Sulfuric acid concentrations: a — 0, b — 59.3, c — 71.3, d — 76.4, e — 79.8, f — 82.9, g — 85.1, h — 90.0, and i — 95.6%.

2,5-Dihydroxybenzoic acid (I). The absorption band of I in region A exhibits a small shift with the increasing sulfuric acid concentration (0—95.8% H_2SO_4). The evaluation of the pK_{BH^+} and m^* values by the excess acidity method [10] in region A was made using the following curve fitting procedure:

$$\varepsilon_{calc.} = \frac{\varepsilon_{BH^+} + \varepsilon_B \cdot 10^{(\log C_{H^+} + pK_{BH^+} + m^* X)}}{1 + 10^{(\log C_{H^+} + pK_{BH^+} + m^* X)}}, \tag{1}$$

minimizing the sum of squares of differences $\sum(\varepsilon_{calc.} - \varepsilon_{exp.})$ using a non-linear regression procedure [11]. This method was applied to the data measured at 49000, 48600 and 48000 cm^{-1}. The respective mean pK_{BH^+} and m^* values are presented in Table 1.

In regions B and C there is a remarkable shift in the absorption spectra observed (see Fig. 1). Therefore the Davis-Geissman treatment [12] followed by the curve fitting procedure (Eq. (1)) was applied. The results obtained are given in Table 2.

Table 1

The pK_{BH^+} and m^* values of the 2,5-dihydroxybenzoic acid in aqueous sulfuric acid solutions calculated by the curve fitting procedure, region A

ν, cm^{-1}	pK_{BH^+}	m^*
49000	−5.88±0.08	0.76±0.02
48600	−5.82±0.06	0.76±0.09
48000	−5.37±0.05	0.70±0.01
Mean [a]	−5.71±0.23	0.74±0.03

[a] Probable errors are given at the confidence level P = 0.95.

Table 2

The pK_{BH^+} and m^* values of the 2,5-dihydroxybenzoic acid in aqueous sulfuric acid solutions calculated by the Davis-Geissman method followed by the curve fitting procedure (Eq. 1), regions B and C

ν_u, cm^{-1}	ν_i, cm^{-1}	pK_{BH^+}	m^*
42000	38600	−6.06±0.11	0.77±0.02
42000	39000	−5.83±0.15	0.73±0.03
42600	38600	−5.84±0.03	0.72±0.01
42600	39000	−5.33±0.08	0.64±0.01
Mean [a]		−5.77±0.30	0.72±0.05
30600	28000	−5.41±0.05	0.70±0.01
30600	28600	−5.47±0.29	0.72±0.05
30600	29000	−5.69±0.08	0.73±0.02
Mean [a]		−5.54±0.20	0.72±0.03

[a] See the footnote to Table 1.

141

3,5-Dihydroxybenzoic acid (II). The absorption band of II in region A shows practically no shift (Fig. 2). This allowed us to apply Eq. (1) to estimating pK_{BH^+} and m^* (see Table 3).

On the other hand, the spectra of II in regions B and C are shifting with the increasing sulfuric acid concentration. This made us apply the Davis-Geissman treatment followed by the curve fitting procedure (Eq. (1)). The results obtained are presented in Table 4.

Table 3

The pK_{BH^+} and m^* values of the 3,5-dihydroxybenzoic acid in aqueous sulfuric acid solutions calculated by the curve fitting procedure, region A

ν, cm^{-1}	pK_{BH^+}	m^*
49000	−6.50±0.17	0.74±0.03
48600	−6.35±0.16	0.72±0.02
Mean [a]	−6.40±0.17	0.73±0.03

[a] See the footnote to Table 1.

Table 4

The pK_{BH^+} and m^* values of the 3,5-dihydroxybenzoic acid in aqueous sulfuric acid solutions calculated by the Davis-Geissman method followed by the curve fitting procedure (Eq. 1), regions B and C

ν_u, cm^{-1}	ν_i, cm^{-1}	pK_{BH^+}	m^*
39600	38000	−7.04±0.05	0.81±0.01
39600	38600	−7.05±0.31	0.81±0.05
40000	38000	−7.19±0.05	0.83±0.01
40000	38600	−7.37±0.13	0.85±0.02
40600	38000	−7.24±0.24	0.84±0.01
40600	38600	−7.31±0.20	0.84±0.03
Mean [a]		−7.23±0.17	0.83±0.03
32600	30600	−6.72±0.10	0.76±0.02
32600	31000	−6.94±0.22	0.78±0.03
33000	30600	−6.93±0.18	0.79±0.03
33000	31000	−7.11±0.11	0.80±0.02
Mean [a]		−6.93±0.20	0.78±0.03

[a] See the footnote to Table 1.

Table 5

The pK_{BH^+} and m^* values of the 3,4,5-trihydroxybenzoic acid in aqueous sulfuric acid solutions calculated by the curve fitting procedure, region A

ν, cm^{-1}	pK_{BH^+}	m^*
47000	−4.86±0.16	0.50±0.04
46600	−5.36±0.15	0.54±0.02
Mean [a]	−5.06±0.30	0.52±0.03

[a] See the footnote to Table 1.

3,4,5-Trihydroxybenzoic acid. Analogically to I and II, in region A the spectra of III show practically no shift with the increasing sulfuric acid concentration. This allowed us to apply directly the curve fitting procedure (Eq. (1)) (see Table 5).

For the base III the spectra in regions B and C are presented by a joint wide and shifting maximum (see Fig. 3). To this maximum the Davis-Geissman treatment followed by the curve fitting procedure was applied. The results obtained are presented in Table 6.

The mean pK_{BH^+} and m^* values presented in Tables 7 and 8 summarize the results of the calculations.

The pK_{BH^+} and m^* values of the 3,4,5-trihydroxybenzoic acid in aqueous sulfuric acid solutions calculated by the Davis-Geissman method followed by the curve fitting procedure (Eq. 1), region B

ν_u, cm^{-1}	ν_i, cm^{-1}	pK_{BH^+}	m^*
36600	31600	-5.67 ± 0.11	0.71 ± 0.02
36600	32000	-5.58 ± 0.13	0.70 ± 0.02
36600	32600	-5.58 ± 0.10	0.70 ± 0.02
37600	31600	-5.42 ± 0.03	0.68 ± 0.06
37600	32000	-5.31 ± 0.06	0.66 ± 0.01
37600	32600	-5.30 ± 0.09	0.66 ± 0.02
Mean [a]		-5.49 ± 0.17	0.69 ± 0.03

[a] See the footnote to Table 1.

The mean pK_{BH^+} values of the hydroxybenzoic acids obtained

Base	Mean values		
	Region A	Region B	Region C
I 2,5-Dihydroxybenzoic	-5.71 ± 0.23	-5.77 ± 0.30	-5.54 ± 0.20
II 3,5-Dihydroxybenzoic	-6.40 ± 0.17	-7.23 ± 0.17	-6.93 ± 0.20
III 3,4,5-Trihydroxybenzoic	-5.06 ± 0.30	-5.49 ± 0.17	
2-Hydroxybenzoic [a]	-5.21 ± 0.03	-5.32 ± 0.25	-5.14 ± 0.20

[a] from [9].

The mean m^* values of the hydroxybenzoic acids obtained

Base	Mean values		
	Region A	Region B	Region C
I 2,5-Dihydroxybenzoic	0.74 ± 0.03	0.72 ± 0.05	0.72 ± 0.03
II 3,5-Dihydroxybenzoic	0.73 ± 0.03	0.83 ± 0.03	0.78 ± 0.03
III 3,4,5-Trihydroxybenzoic	0.52 ± 0.03	0.69 ± 0.03	
2-Hydroxybenzoic [a]	0.71 ± 0.01	0.72 ± 0.05	0.69 ± 0.04

[a] from [9].

On the whole, the basicity constant values calculated for the different spectral regions show relatively good coincidence (Table 7). But in the case of II and III the non-shifting band A yields more positive results. Those discrepancies may be explained as follows. For HBA the molar absorptivities of the protonated and neutral forms depend on the medium acidity. By applying the Davis-Geissman method [12] for regions B and C, we partly remove the medium effect and in further calculations of pK_{BH^+} values operate with data which describe the "refined" protonation process. But in region A, the protonation constant value is obtained from "raw" spectral data without any elimination of the medium effect. This may distort the final result. The application of the Davis-Geissman method [12] seems to have some advantages in calculations of the basicity parameters of HBA, and the results obtained in regions B and C may be considered the most reliable.

DISCUSSION

Analyzing the dependence $\varepsilon = f(\% H_2SO_4)$ (see Figs. 4—6) we can estimate the H_2SO_4 concentrations at which the weak bases studied become half-protonated (see Table 9).

<div align="right">Table 9</div>

The half-protonation of hydroxybenzoic acids in aqueous sulfuric acid

Concentration, %	2,5-Dihydroxybenzoic acid	3,5-Dihydroxybenzoic acid	3,4,5-Trihydroxy-benzoic acid
H_2SO_4	78—79	87—88	80—81

More information about the protonation of HBA is presented in the plots ε $vs.$ $\% H_2SO_4$:
(i) the protonation of II is perhaps not complete in the most concentrated sulfuric acid solutions used in our experiment: when the H_2SO_4 concentration is higher than 93%, the plot $\varepsilon = f(\% H_2SO_4)$ only begins to curve (see Fig. 4);
(ii) III is more basic than II, because in concentrated H_2SO_4 solutions the ε values become stabilized (Fig. 5);
(iii) I shows an interesting and unusual behavior with the increasing of the H_2SO_4 concentration: at the sulfuric acid concentration of 86—87% most of the plots $\varepsilon = f(\% H_2SO_4)$ have a clearly noticeable extremum, and the ε value does not remain constant after achieving its extreme value but remarkable changes occur in it (Fig. 6).
The protonation site of the HBA studied remains open. In the papers [1, 2, 5] dealing with the basicity of the substituted benzoic acids, the carboxyl group has been considered a basicity center. But some preliminary ^{13}C NMR experiments carried out for this study with the 3,5-dihydroxybenzoic acid in sulfuric acid—water mixtures have led us to the conclusion that the 3,5-dihydroxybenzoic acid protonates probably on the hydroxyl groups. From the UV-absorption spectra the pK_{BH^+} and m^* values of four HBA (including the salicylic acid [9]) were calculated; but we would like to avoid making any final conclusion about the basicity center of HBA till supplementary NMR-spectroscopic information will be available.
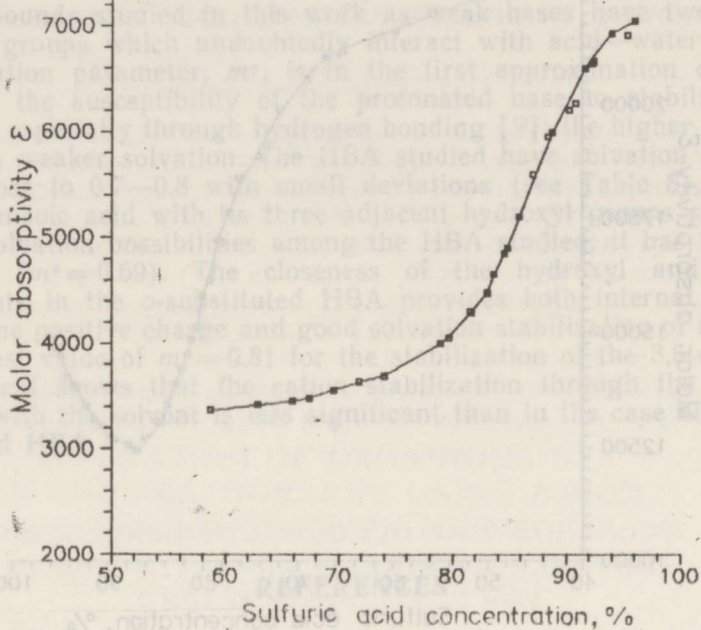
144

The question of solvation is of great interest in the case of HBA. The compounds studied in this work as weak bases have two or more hydroxyl groups which undoubtedly interact with acid—water mixtures. The solvation parameter, m^*, is in the first approximation considered to reflect the susceptibility of the protonated base to stabilization by solvation, mainly through hydrogen bonding [9]. The higher m^* values indicate a weaker solvation. The HBA studied have solvation parameter values close to 0.7—0.8 with small deviations (see Table 5). 3,4,5-Tri-hydroxybenzoic acid with its three adjacent hydroxyl groups reveals the highest solvation possibilities among the HBA studied, it has the lowest m^* value $m^* = 0.69$. The closeness of the hydroxyl and carboxyl substituents in the o-substituted HBA provides both internal delocalization of the positive charge and good solvation stabilization of the cation. The highest value of $m^* = 0.81$ for the stabilization of the 3,5-dihydroxy-benzoic acid shows that the cation stabilization through the hydrogen bonding with the solvent is less significant than in the case of the other protonated HBA.

Fig. 4. Molar absorptivity of the 3,5-dihydroxybenzoic acid *vs.* per cent of sulfuric acid. $\nu = 38000$ cm^{-1}.
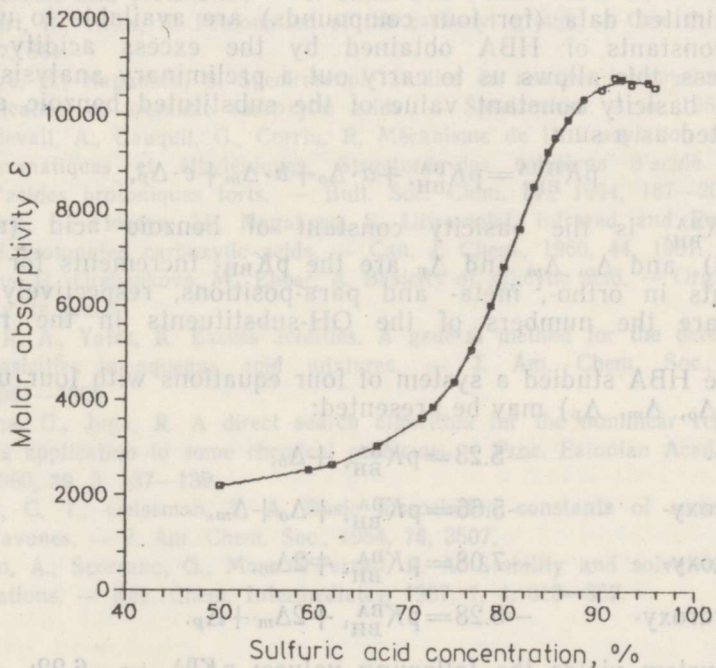

Fig. 5. Molar absorptivity of the 3,4,5-trihydroxybenzoic acid *vs.* per cent of sulfuric acid. $\nu = 32600$ cm^{-1}.
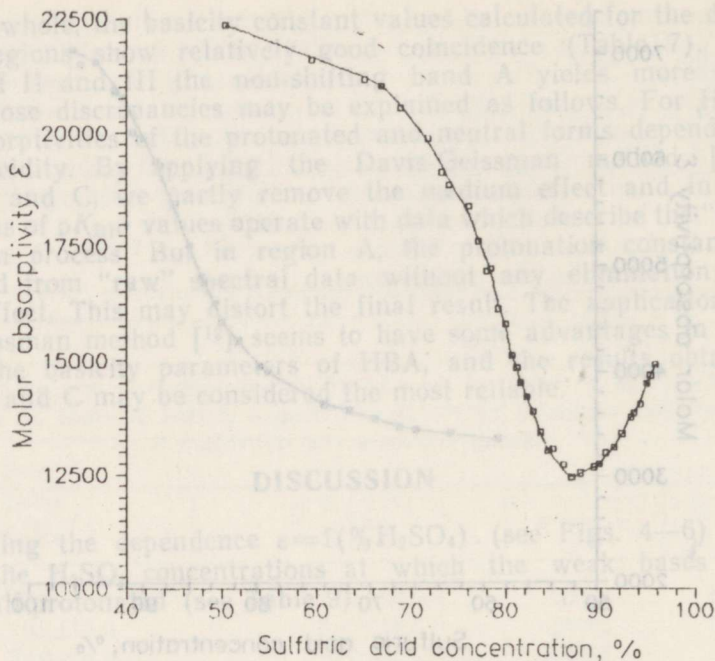
Fig. 6. Molar absorptivity of the 2,5-dihydroxybenzoic acid *vs.* per cent of sulfuric acid. $\nu = 47000$ cm^{-1}.

Only limited data (for four compounds) are available to us on the basicity constants of HBA obtained by the excess acidity method. Nevertheless, this allows us to carry out a preliminary analysis of these data. The basicity constant value of the substituted benzoic acid may be presented as a sum

$$pK_{BH^+}^{HBA} = pK_{BH^+}^{BA} + a \cdot \Delta_o + b \cdot \Delta_m + c \cdot \Delta_p, \tag{2}$$

where $pK_{BH^+}^{BA}$ is the basicity constant of benzoic acid (a parent compound), and Δ_o, Δ_m and Δ_p are the pK_{BH^+} increments for the OH-substituents in ortho-, meta- and para-positions, respectively. The a, b and c are the numbers of the OH-substituents in the respective positions.

For the HBA studied a system of four equations with four unknowns ($pK_{BH^+}^{BA}$, Δ_o, Δ_m, Δ_p) may be presented:

2-hydroxy- $-5.23 = pK_{BH^+}^{BA} + \Delta_o,$ (3)

2,5-dihydroxy- $-5.66 = pK_{BH^+}^{BA} + \Delta_o + \Delta_m,$ (4)

3,5-dihydroxy- $-7.08 = pK_{BH^+}^{BA} + 2\Delta_m,$ (5)

3,4,5-trihydroxy- $-5.28 = pK_{BH^+}^{BA} + 2\Delta_m + \Delta_p.$ (6)

This system yields the following values: $pK_{BH^+}^{BA} = -6.22$; $\Delta_o = 0.99$, $\Delta_m = -0.43$, $\Delta_p = 1.80$. This means that the o- and p-hydroxyl groups increase the basicity of benzoic acid derivatives and m-hydroxyl operates in the opposite direction.

146

The question of solvation is of great interest in the case of HBA. The compounds studied in this work as weak bases have two or more hydroxyl groups which undoubtedly interact with acid—water mixtures. The solvation parameter, m^*, is in the first approximation considered to reflect the susceptibility of the protonated base to stabilization by solvation, especially through hydrogen bonding [13]; the higher m^* values indicate a weaker solvation. The HBA studied have solvation parameter values close to 0.7—0.8 with small deviations (see Table 8). 3,4,5-Trihydroxybenzoic acid with its three adjacent hydroxyl groups reveals the highest solvation possibilities among the HBA studied: it has the lowest m^* value ($m^* = 0.69$). The closeness of the hydroxyl and carboxyl substituents in the o-substituted HBA provides both internal delocalization of the positive charge and good solvation stabilization of the cation. The highest value of $m^* = 0.81$ for the stabilization of the 3,5-dihydroxybenzoic acid shows that the cation stabilization through the hydrogen bonding with the solvent is less significant than in the case of the other protonated HBA.

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MÕNINGATE HÜDROKSÜBENSOEHAPETE ALUSELISUSE UURIMINE UV-SPEKTROFOTOMEETRILISE MEETODIGA

Marina GREBENKOVA, Ülo HALDNA

On uuritud kolme hüdroksübensoehappe — 2,5-dihüdroksübensoehappe, 3,5-dihüdroksübensoehappe ning 3,4,5-trihüdroksübensoehappe aluselisust. Selleks on mõõdetud loetletud ainete UV-neeldumisspektreid väävelhappe vesilahuses (0—96% mass. H_2SO_4). Spektrid mõõdeti piirkonnas 52 000—28 000 cm^{-1}, kus leiti kaks kuni kolm neeldumisriba. Uuritud ainete aluselisuse parameetrite (pK_{BH^+} ja m^*) arvutamiseks kasutati Coxi—Yatesi liighappesuse meetodi, kõverate sõltuvuste parameetrite hindamise meetodi ning Davise—Geissmani meetodi kombinatsiooni. Leitud aluselisuse parameetrid on järgmised: 2,5-dihüdroksübensoehappel $pK_{BH^+} = -5{,}67$ ja $m^* = 0{,}72$; 3,5-dihüdroksübensoehappel $pK_{BH^+} = -7{,}08$ ja $m^* = 0{,}81$; 3,4,5-trihüdroksübensoehappel $pK_{BH^+} = -5{,}49$ ja $m^* = 0{,}69$.

ИССЛЕДОВАНИЕ ОСНОВНОСТИ НЕКОТОРЫХ ГИДРОКСИБЕНЗОЙНЫХ КИСЛОТ МЕТОДОМ УФ-СПЕКТРОФОТОМЕТРИИ

Марина ГРЕБЕНКОВА, Юло ХАЛДНА

Проведено исследование основности трех гидроксибензойных кислот (2,5-дигидрокси-, 3,5-дигидрокси- и 3,4,5-тригидроксибензойной) на основе УФ-спектров поглощения в водных растворах серной кислоты (0—96% мас. H_2SO_4). Спектры были измерены в диапазоне 52 000—28 000 cm^{-1}, где присутствуют две-три полосы поглощения. Для расчета константы основности (pK_{BH^+}) и сольватационного параметра (m^*) исследуемых соединений использована комбинация трех методов: метода избыточной кислотности Кокса—Эйтса, метода наилучшего совпадения расчетной и экспериментальной кривых и метода Девиса—Гейссмана. В результате расчетов получены следующие значения параметров основности: 2,5-диметилрезорцин: $pK_{BH^+} = -5{,}67$, $m^* = 0{,}72$; 3,5-диметилрезорцин: $pK_{BH^+} = -7{,}08$, $m^* = 0{,}81$; 3,4,5-триметилрезорцин: $pK_{BH^+} = -5{,}49$, $m^* = 0{,}69$.