

PROTONATION OF CITRACONIC AND GLUTACONIC ACID IN PERCHLORIC ACID MEDIA

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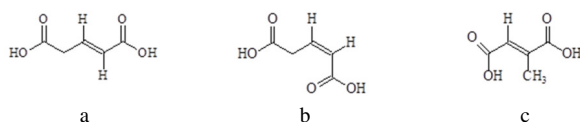
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ABSTRACT: The protonation process of citraconic and glutaconic acid in perchloric acid media was followed using the method of UV spectroscopy. The observed changes in the UV spectra of investigated acids confirmed that the protonation process in perchloric acid with concentration from 5 to 10 mol/dm³ occurred. Glutaconic acid behaved as weak organic base in perchloric acid media and existed in its monoprotinated form. On the other hand, citraconic acid existed in its protonated form and as protonated anhydride at higher perchloric acid concentration. Using the absorbance data the thermodynamic dissociation constants were calculated applying the methods of Yates and McClelland, Bunnett and Olsen, and the "excess acidity" function method. The solvation parameters m , m^* and ϕ were evaluated, as well. In order to correct the medium effect the method of characteristic vector analysis was applied. The possible site where the protonation may take place was discussed using the partial atomic charge values determined according to AM1 and PM3 semiempirical methods.

KEYWORDS: citraconic acid, glutaconic acid, UV spectroscopy, thermodynamic dissociation constants, AM1 and PM3 semiempirical methods

INTRODUCTION

The structural formulas of citraconic (*cis*-2-methyl-1,2-ethylenedicarboxylic acid) and glutaconic (pent-2-enedioic acid) acid are shown in Scheme 1.



Scheme 1. Structural formulas of *trans*-glutaconic (a), *cis*-glutaconic (b) and citraconic acid (c)

Glutaconic acid exists in two forms: *cis*-glutaconic and *trans*-glutaconic acid. In the aqueous solutions *cis*-glutaconic acid undergoes isomerization and it is transformed into the *trans*-form which is more stable [1]. Glutaconic acid is important industrial substance because of their wide practical application. For instance, this acid can be used as monomer for production of biodegradable polyesters in chemical industry. Furthermore, glutaconic acid by condensation with suitable α,ω -diaminoalkanes participate in formation of polyamides [2]. Citraconic acid is used in the production of synthetic resins and polymers [1]. When the anhydride of citraconic acid reacts with primary amines an amide bond with a terminal carboxyl group can be formed. This reaction can be reversed in acidic condition *i.e.* pH from 3 to

4. It suggests that this anhydride can be used to block primary amine groups in alkaline conditions when pH value is between 7 and 9 [3].

The unsaturated dicarboxylic acids were studied by many authors, and some of them investigated the acid-base behavior of citraconic and glutaconic acid [4]-[7]. The protonation process of citraconic and glutaconic acid in sulfuric acid media was studied by several authors and the dissociation constants values (pK_{BH}^+) of protonated acids were determined, as well [5]-[8]. Knowing the pK_{BH}^+ values of carboxylic acids is important in order to understand the mechanisms of the reactions in which they take part [9]. However, there is no literature data about thermodynamic dissociation constants values of citraconic and glutaconic acid determined in perchloric acid media. In order to investigate the influence of the strength of the acid and its anion on the protonation process it is important to use different mineral acids for protonation.

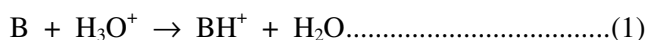
Taking into consideration that thermodynamic pK_{BH}^+ values are important parameters for weak organic acids the purpose of this work was to follow the protonation process of citraconic and glutaconic acid in perchloric acid media by means of UV spectroscopy. The changes in the spectra can be used for determination of thermodynamic dissociation constant values of protonated acids. At the same time, using the semiempirical AM1 and PM3 quantum

chemical methods the possible protonation site in the molecules of the investigated acids can be predicted [10], [11].

EXPERIMENTAL

Chemicals and equipment: The stock solutions were prepared by dissolving a known amount of the investigated acids in redistilled water. The concentration of citraconic acid in the stock solutions was $9.8 \cdot 10^{-5} \text{ mol/dm}^3$, while that of glutaconic acid was $8.3 \cdot 10^{-5} \text{ mol/dm}^3$. Two series of test solutions with constant concentration of investigated organic acids were prepared. The concentration of perchloric acid in the test solutions was varied between 1 mol/dm^3 and 11 mol/dm^3 . The UV spectra of the two series of solutions were recorded at room temperature in the wavelength region from 190 nm to 290 nm with 1 nm resolution, 24 hours after preparation of the test solutions. The absorbance data at the following wavelengths: 198, 206, 214 and 220 nm were used for calculation of the $\text{p}K_{\text{BH}^+}$ values of glutaconic acid. The wavelengths were selected around the maximum of the absorption band. The molar absorption coefficient values of the unprotonated form of glutaconic acid were determined at perchloric acid concentration of 1 mol/dm^3 from the absorbance data at the same wavelengths. It was considered that at this mineral acid concentration glutaconic acid existed in its unprotonated form. The molar absorption coefficient values of protonated form of glutaconic acid were determined when the perchloric acid concentration was 11 mol/dm^3 , because the protonation process of glutaconic acid at this concentration was completed. All used substances were of analytical grade p.a (Alkaloid and Merck). The concentration of perchloric acid was determined by titration with a standard solution of sodium hydroxide. The UV spectra were recorded on a Varian Cary spectrophotometer using quartz cell with 1 cm length, at room temperature. All calculations were performed by Microsoft Excel computer program.

Calculation of the $\text{p}K_{\text{BH}^+}$ values: It is well known that the investigated carboxylic acids in water behave as proton donors, while in strong mineral acid media as proton acceptors. The protonation equilibria of these substances can be presented with the equation (1).



The $\text{p}K_{\text{BH}^+}$ values in highly acidic media can be evaluated by Hammett [12] equation (2) in the following form:

$$\text{p}K_{\text{BH}^+} = H_0 + \log I \dots \dots \dots (2)$$

where, $\text{p}K_{\text{BH}^+}$ is the dissociation constant of protonated form of the acid, H_0 is Hammett acidity function, I is a ratio between the concentration of the protonated and unprotonated form of the acid (ionization ratio).

When the absorbance values of protonated and unprotonated forms are measurable the ionization ratio can be calculated as $\log I = c(\text{BH}^+)/c(\text{B})$. B is the set of primary nitroanilines that serve as reference bases which can be protonated in strongly mineral acid media. The Hammett acidity function (H_0) was no valid for all types of weak bases and it was upgraded by several authors. Bunnett and Olsen [13] calculated the thermodynamic dissociation constants according to the equation (3).

$$\log I + H_0 = \phi[H_0 + \log c(\text{H}^+)] + \text{p}K_{\text{BH}^+} \dots \dots \dots (3)$$

where, ϕ is a parameter which characterizes the changing activity coefficient behavior of bases with changing acidity.

Using the equation (3) necessity of different acidity functions to characterize the protonation process of different bases was reduced to one acidity function, *i.e.*, Hammett acidity function. The method of Yates and McClelland also can be used to determine the thermodynamic $\text{p}K_{\text{BH}^+}$ values [14]. In this case, the calculations can be made by the equation (4).

$$\log I = -mH_0 + \text{p}K_{\text{BH}^+} \dots \dots \dots (4)$$

A plot of $\log I$ vs. $-H_0$ gives a straight line with slope m , whose value is about 1. Actually, the $\text{p}K_{\text{BH}^+}$ values should be calculated using the acidity functions which make possible the best slope of the dependence of $\log I$ vs. H_0 , *i.e.*, slope closest to unity. This suggest that the protonation process is favored compared to the solvation process and the $\text{p}K_{\text{BH}^+}$ values calculated by this method would be more accurate. Furthermore, the method of Cox and Yates [15], also known as the "excess acidity" function method (Eq. 5), was applied to determine the thermodynamic $\text{p}K_{\text{BH}^+}$ values and the values of the solvation parameter m^* .

$$\log I - \log c_{\text{H}^+} = m^*X + \text{p}K_{\text{BH}^+} \dots \dots \dots (5)$$

where, m^* expresses the hydrogen-bonding solvation of the protonated base. X is excess acidity function which represents the difference between the observed acidity and that which the system would have if it was ideal.

The excess acidity function X is defined using the obtained data of the ionization ratio of 76 weak bases in 0–78% aqueous perchloric acid solutions [16]. These bases included compounds where the protonation centre is the atoms of N, C, O and S. Hence, using the acidity function X the values of the dissociation constants for different bases could be determined in aqueous perchloric acid solutions. The "excess acidity" function X method is mostly used for determination of pK_{BH^+} values of organic bases in strong mineral acid media [16].

RESULTS AND DISCUSSION

UV spectra of citraconic and glutaconic acid:

The UV spectra of citraconic and glutaconic acid were recorded at the wavelength region from 190 to 280 nm, as it is shown in the Figs. 1 and 2, respectively.

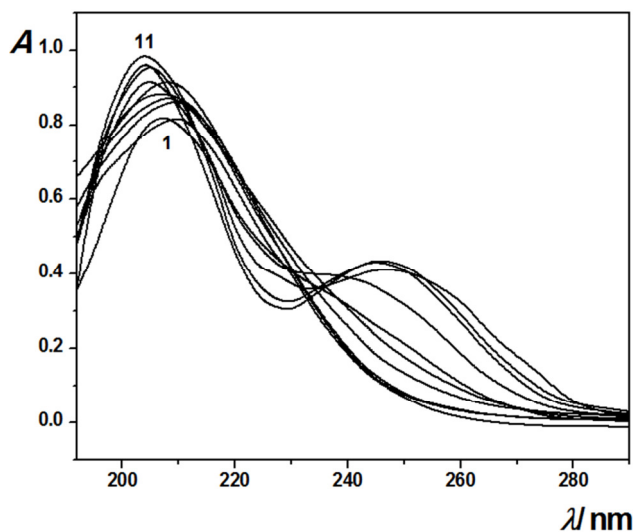


Fig. 1. Experimental UV spectra of citraconic acid ($c = 9.8 \cdot 10^{-5}$ mol/dm³) in perchloric acid media ($c(\text{HClO}_4) = 1$ mol/dm³ (spectrum 1), $c(\text{HClO}_4) = 11$ mol/dm³ (spectrum 11))

At lower perchloric acid concentration (below 5 mol/dm³) in the spectrum of citraconic acid a single band at 212 nm (marked with 1, in the Fig. 1) appeared (See Fig. 1). When the concentration of perchloric acid increased this band shifted monotonic to 204 nm (marked with 11 in the Fig. 1) and its intensity increased. At higher perchloric acid concentration a new band at 246 nm appeared. These two absorption bands are due to the $\pi \rightarrow \pi^*$ electron transitions. In accordance with the previous investigations [5]–[8] it was expected that the citraconic acid exists in the protonated form and protonated anhydride, as a result of partial dehydration of the formed protonated acid [17].

It suggested that the reaction of protonation and dehydration took place at the same time. Hence, the absorption band which appeared at 246 nm (See Fig. 1) was due to existence of the anhydride in the solution. The existence of two bands in the spectrum of citraconic acid was in agreement with the literature data which confirmed that for some organic acid at higher mineral acid concentration anhydrides are formed [17], [18]. In the spectrum of glutaconic acid a single absorption band around 214 nm (marked with 1 in the Fig. 2) appeared. When the perchloric acid concentration increased the hypsochromic effect was observed, similarly as it was case with the changes in the position of the spectral band of citraconic acid, and the intensity of this band insignificantly increased. When the concentration of perchloric acid was 11 mol/dm³ the band was placed at 204 nm (marked with 11 in the Fig. 2).

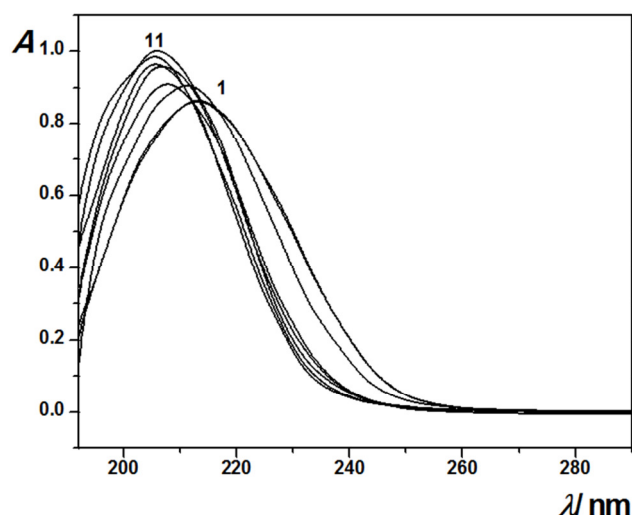


Fig. 2. Experimental UV spectra of glutaconic acid ($c = 8.3 \cdot 10^{-5}$ mol/dm³) in perchloric acid media ($c(\text{HClO}_4) = 1$ mol/dm³ (spectrum 1), $c(\text{HClO}_4) = 11$ mol/dm³ (spectrum 11))

On the basis of these results and previous studies [4]–[8], the existence of one isosbestic point in the UV spectra of citraconic and glutaconic acid was expected. However, its position could not be established clearly, because of the influence of the solvent. In order to determine the precise position of the isosbestic points, and to separate the influence of the solvent the experimental spectra were reconstructed using the method of characteristic vector analysis (CVA) [19]. The obtained reconstructed spectra of citraconic and glutaconic acid are shown in the Figs. 3 and 4, respectively.

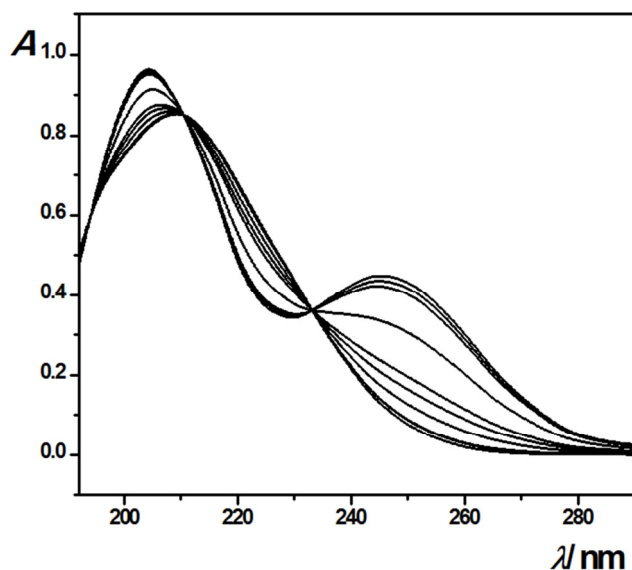


Fig. 3. Reconstructed UV spectra of citraconic acid ($c = 9.8 \cdot 10^{-5}$ mol/dm³) in perchloric acid media

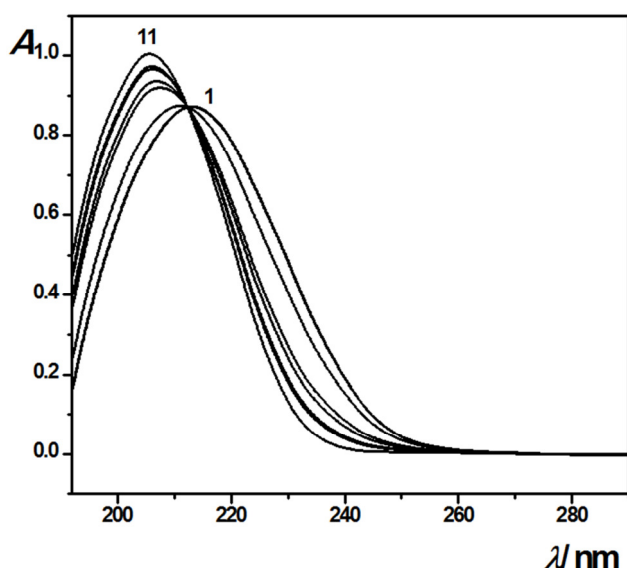


Fig. 4. Reconstructed UV spectra of glutaconic acid ($c = 8.3 \cdot 10^{-5}$ mol/dm³) in perchloric acid media

As it can be seen from the Fig. 3, two isosbestic points existed in the spectrum of citraconic acid, the first one at 210 nm and the second one at 234 nm. It means that there were three forms able to absorb UV radiation in the system: the acid in its unprotonated form, the protonated form of the acid and the protonated anhydride. Because of that, it was complicated to determine the pK_{BH^+} values of citraconic acid. Hence, the protonation process of citraconic acid was characterized only qualitatively. The existence of one isosbestic point at 212 nm in the spectrum of glutaconic acid (See Fig. 4) suggested that in the reaction system two forms were present, *i.e.*, the unprotonated

and protonated form of glutaconic acid. This result was in agreement with the investigations made for similar systems [4-8]. Furthermore, the one step of protonation of glutaconic acid was confirmed with the dependence of the absorbance at 220 nm on perchloric acid concentration. This dependence had a sigmoidal shape, *i.e.*, sigmoidal curve, S (See Fig. 5).

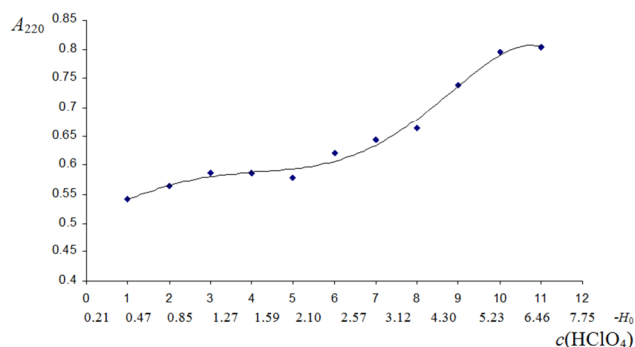


Fig. 5. The dependence of the absorbance ($\lambda = 220$ nm) of glutaconic acid ($c = 8.3 \cdot 10^{-5}$ mol/dm³) on perchloric acid concentration

From the Fig. 5 it could be seen that the S curve had only one step. It confirmed that only one carboxylic group was protonated. When the concentration of perchloric acid was below 6 mol/dm³ ($H_0 = -2.10$) the glutaconic acid existed in its unprotonated form, while at perchloric acid concentration up to 10 mol/dm³ ($H_0 = -5.23$) the protonated form of the acid was formed. In agreement with previous investigations of similar organic acids obtained in mineral acid media and on the base of the results presented in this investigation, it was clear that in perchloric acid media the protonation process of citraconic and glutaconic acid took place [4]-[8].

Partial atomic charges: The exact place of protonation of the investigated organic acid is an important question. In order to establish the site of protonation of some organic acids (fumaric, maleic, acnitic, glutaconic, citraconic and mezaconic acid) many authors used different methods such as: ultra-violet, infrared, Raman, mass and NMR spectroscopy [20]-[23]. Most of them suggested that the protonation takes place on the oxygen of the carbonyl group [18], [24]-[26]. The possible protonation reaction of glutaconic and citraconic acid in perchloric acid media can be predicted according to the literature data and the calculated values of the partial charges using semiempirical methods [27]. In this work AM1 (Austin Model 1) and PM3 (Parametric Method 3) semiempirical methods were used for optimization of the geometry of investigated acids [10], [11]. For that

purpose HyperChem computer program was used [28]. The partial atomic charges of atoms which are possible protonation centers in the molecule of the investigated acids were determined by AM1 (Austin Model 1) and PM3 (Parameterized Model 3) methods (Tables 1-3).

Table 1. Atomic charges of *cis*-glutaconic acid calculated by AM1 and PM3 semiempirical methods

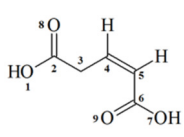
	protonation site	AM1	PM3
	1 O	-0.3114	-0.3045
2 C	0.3089	0.3815	
3 C	-0.1560	-0.0869	
4 C	-0.0625	-0.0353	
5 C	-0.2031	-0.1940	
6 C	0.3359	0.4187	
7 O	-0.3081	-0.3011	
8 O	-0.3640	-0.3971	
9 O	-0.3768	-0.4098	

Table 2. Atomic charges of *trans*-glutaconic acid calculated by AM1 and PM3 semiempirical methods

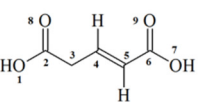
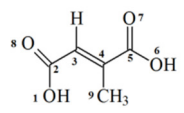
	protonation site	AM1	PM3
	1 O	-0.3178	-0.3110
2 C	0.3064	0.3783	
3 C	-0.1455	-0.0769	
4 C	-0.0730	-0.0480	
5 C	-0.1972	-0.1909	
6 C	0.3383	0.4159	
7 O	-0.3145	-0.3052	
8 O	-0.3475	-0.3826	
9 O	-0.3577	-0.3945	

Table 3. Atomic charges of citraconic acid calculated by AM1 and PM3 semiempirical methods

	protonation site	AM1	PM3
	1 O	-0.3060	-0.3003
2 C	0.3342	0.4117	
3 C	-0.1400	-0.1287	
4 C	-0.0269	-0.0372	
5 C	0.3290	0.4045	
6 O	-0.3036	-0.2953	
7 O	-0.3489	-0.3895	
8 O	-0.3549	-0.3917	
9 C	-0.2030	-0.0918	

According to the values of partial atomic charge (Tables 1 and 2) the protonation process of glutamic acid occurred on the oxygen of the carbonyl group

which is closer to the double bond (marked with 9) probably as a result of higher electronic density on that place in the molecule. The citraconic acid was protonated on the carbonyl oxygen of the carboxylic group marked with 8 (Table 3). The similar atomic charge values were obtained for the oxygen atom of the carbonyl group which is closer to the methyl group (marked with 7) probably because of its positive inductive effect.

Determination of the pK_{BH}^+ values: The protonation process of glutamic acid was quantitatively characterized with the pK_{BH}^+ values calculated using the following methods: Bunnett and Olsen [13], Yates and McClelland [14], and Cox and Yates [15] (equations (3-5)). The pK_{BH}^+ values could be calculated using the data of the acidity functions H_0 and X which are known from the literature [12], [15], [29]-[31] and the ionization ratio between the concentration of protonated and unprotonated form of the acid, I . This ratio was determined from the absorbance data according to Beer's law [32], [33]. Actually, the concentrations of protonated and unprotonated form of the acids were determined from absorbance data (experimental and reconstructed) using an overdetermined system of four equations (absorbance values) with two unknown parameters (concentration of unprotonated and protonated form). The molar absorption coefficient values (needful for calculation of the ionization ratio) were obtained by measuring the absorbance values at the concentration of perchloric acid when glutamic acid existed in its protonated and unprotonated form. The molar absorption coefficients, absorbance data, and the ionization ratio values at the selected wavelengths of glutamic acid are given in Table 1.

There is no acidity functions determined when carboxylic acids were used as indicators. Thus, the pK_{BH}^+ values could be determined using the acidity functions obtained with compounds which are protonated at the same protonation center as the investigated acids [34]. When the method of Yates and McClelland [14] was used the calculations were made with the amide acidity function (H_A) instead of H_0 . The pK_{BH}^+ obtained in this way was close to those calculated according to the "excess acidity" function method [15]. Because of that, the H_A acidity function was considered as more appropriate for calculation of the pK_{BH}^+ values. In this case it was expected that the slope parameter would have the value equal to unity.

The pK_{BH}^+ values of glutamic acid also were determined graphically using the method of Davis and Geissman [35]. Namely, when $\log I = 0$, it is as-

sumed that the acid is half protonated, then $H_0 = (H_0)_{1/2}$. These values multiplied with the slope parameter m gave the graphically value of the pK_{BH^+} , *i.e.* $pK_{BH^+} = m \cdot (H_A)_{1/2}$. The values of the solvation parameters m , m^* and ϕ , the correlation coefficients, the standard deviation (SD) and relative standard deviation (RSD) were calculated, as well. The dependence of $\log I$ on H_0 is linear with slope which depend on

the method of calculation, and with an intercept equal to the graphic value of the thermodynamic dissociation constant. In the "excess acidity" function method the dependence of $\log I - \log c_{H^+}$ vs. X was linear. The dependence of $\log I$ on H_A (Yates and McClelland method) and $\log I - \log c_{H^+}$ on X (Cox and Yates method) for glutaconic acid in perchloric acid media is shown in the Figs. 6 and 7, respectively.

Table 4. The spectrophotometric data of glutaconic acid ($c = 8.3 \cdot 10^{-5}$ mol/dm³) in perchloric acid media, and values of $\log I$ (reconstructed spectra)

$c(\text{HClO}_4)$ [mol/dm ³]	$\log I$	A_{198}	A_{205}	A_{214}	A_{220}
1		0.5018	0.7418	0.8683	0.7924
2		0.8815	0.9953	0.8174	0.5423
3		0.7547	0.9731	0.8013	0.5747
4		0.7832	0.9942	0.8212	0.5320
5	-1.185	0.8363	1.0108	0.8573	0.4580
6	-0.731	0.7207	0.9598	0.8542	0.5325
7	-0.219	0.6871	0.8931	0.8263	0.6259
8	0.284	0.5589	0.8871	0.8488	0.6827
9	0.791	0.5280	0.8409	0.8935	0.7599
10	1.602	0.5140	0.7534	0.8672	0.7913
11		0.5087	0.7218	0.8354	0.8047
	ϵ_B	95635	104791	89528	60968
	ϵ_{BH^+}	60234	90933	104653	95509

*The molar absorption coefficient values (ϵ [dm³ mol⁻¹ cm⁻¹]) of unprotonated and protonated form of glutaconic acid

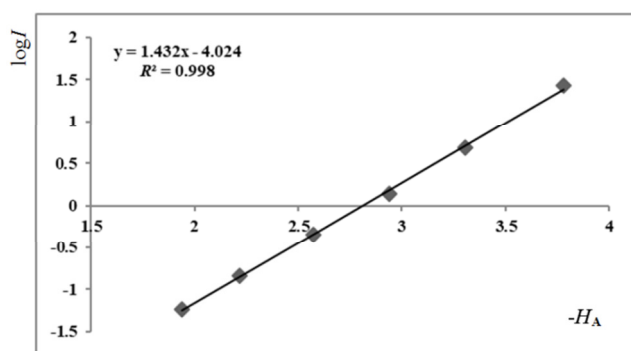


Fig. 6. The dependence of $\log I$ on H_A for glutaconic acid

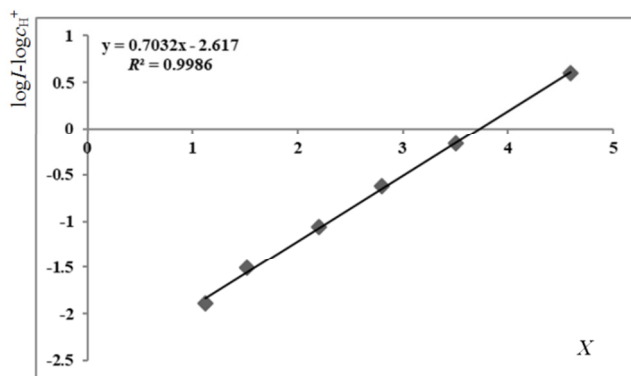


Fig. 7. The dependence of $\log I - \log c_{H^+}$ on X for glutaconic acid

As it was mentioned before H_A is the most adequate one for determination of the pK_{BH^+} values for dicarboxylic acids, *i.e.*, using this function the slope value closest to unity was obtained (See Fig. 6). The values of the numerically and graphically obtained thermodynamic dissociation constants (pK_{BH^+}) with their confidence interval at 95% confidence levels, the slope parameters (m , m^* and ϕ) and statistical data are presented in Table 2.

The thermodynamic dissociation constants (pK_{BH^+}) determined according to Bunnett and Olsen had more negative values compared to those calculated by other methods (see Table 5). As a result of different grade of solvation of the used bases the slope parameter ϕ was not equal to unity. This parameter had positive value which means that the solvation of glutaconic acid was more pronounced than that of Hammett's indicators used to set up the H_0 scale [12]. The values of the solvation parameter m^* ("excess acidity" function method) for glutaconic acid were similar to those obtained for amides ($m^* = 0.51 \pm 0.07$) which additionally confirmed that the amide acidity function was the most suitable one for calculation of the pK_{BH^+} for this acid [13]. Therefore,

in Yates and McClelland's equation (Eq. 3) H_A instead of H_0 was used [12]. As a result of that the values of the slope parameter m were close to unity, and the pK_{BH^+} values can be considered as thermodynamic dissociation constants. The pK_{BH^+} values calculated with this method were similar to those calculated according to the "excess acidity" function method [13]. It suggested that the method of Yates and McClelland

was more reliable for determination of pK_{BH^+} values than the method of Bunnett and Olsen. The pK_{BH^+} values of glutaconic acid determined in perchloric acid media were more positive compared to pK_{BH^+} values which we had reported in sulfuric acid media [8]. It was expected because perchloric acid is stronger than sulfuric acid as a result of the influence of the anion.

Table 5. Thermodynamic pK_{BH^+} values of glutaconic acid (experimental and reconstructed spectra)

experimental spectra			reconstructed spectra		
"excess acidity" function method					
pK_{BH^+} (numerically)	pK_{BH^+} (graphically)	m^*	pK_{BH^+} (numerically)	pK_{BH^+} (graphically)	m^*
-2.61 ± 0.027 SD = 0.034 RSD = 1.31	-2.62	0.70	-2.66 ± 0.017 $s = 0.022$ $V = 0.81$	-2.67	0.67
Bunnett and Olsen					
pK_{BH^+} (numerically)	pK_{BH^+} (graphically)	ϕ	pK_{BH^+} (numerically)	pK_{BH^+} (graphically)	ϕ
-3.81 ± 0.035 $s = 0.039$ $V = 1.03$	-3.80	0.57	-3.92 ± 0.031 $s = 0.044$ $V = 1.12$	-3.81	0.51
Yates and McClelland					
pK_{BH^+} (numerically)	pK_{BH^+} (graphically)	m	pK_{BH^+} (numerically)	pK_{BH^+} (graphically)	m
-2.83 ± 0.043 $s = 0.02$ $V = 1.22$	-2.80	1.09	-2.75 ± 0.032 $s = 0.060$ $V = 1.11$	-2.73	1.04

CONCLUSION

The protonation reaction of glutaconic acid took place in perchloric acid media, *i.e.*, this acid existed in its protonated form at perchloric acid concentration up to 10 mol/dm^3 . On the other side, citraconic acid at higher perchloric acid concentration existed in its protonated form and as a protonated anhydride, as well. Thus, the thermodynamic dissociation constants were determined for glutaconic acid, while the protonation process of citraconic acid was characterized only qualitatively. There was no significant difference between the numerically and graphically calculated pK_{BH^+} values which was statistically confirmed. The differences between the thermodynamic dissociation constants obtained from the experimental and the reconstructed spectra were also insignificant. It indicated that there was a little influence of the solvent on the appearance of the spectra compared to the effect of the protonation reaction. The correlation coefficient values of the dependence of $\log I$ on H_A (amide acidity function) or X ("excess acidity" function method) used acidity function were between 0.995 and 0.998. This suggested a good correlation

between the values used for calculation of the pK_{BH^+} and the slope parameter values obtained using the different acidity functions.

REFERENCES

- [1] H. Warson, C. A. Finch, *Applications of synthetic resin lattices*, John Wiley & Sons Ltd., Chichester, England, Vol.135, 2001.
- [2] S. Kind, W. K. Jeong, H. Schröder, C. Wittmann, "Systems-wide metabolic pathway engineering in *Corynebacterium glutamicum* for bio-based production of diaminopentane", *Metab. Eng.*, vol. 12, pp. 341-351, 2010.
- [3] M. H. Klapper, I. M. Klotz, "Acylation with dicarboxylic acid anhydrides", *Methods in Enzymol.*, vol. 25, pp. 531-532, 1972.
- [4] I. Spirevska, L. Šoptrajanova, B. Andonovski, "Protonation of itaconic acid in sulfuric and perchloric acid", *Bull. Chem. Technol. Macedonia*, vol. 8, pp. 151-156, 1990.
- [5] L. Šoptrajanova, I. Spirevska, "Behaviour of citraconic and mesaconic acid in strong acid media", *Bull. Chem. Technol. Macedonia*, vol. 10, pp. 21-26, 1991.
- [6] I. Spirevska, L. Šoptrajanova, K. Jankovska, B. Andonovski, "UV study of the formation of superacids in a sulfuric acid medium", *J. Mol. Struct.*, vol. 293, pp. 93-96, 1993.
- [7] K. Jankoska, L. Šoptrajanova, I. Spirevska, "Protonation of citraconic and mesaconic acid in aqueous and ethanolic so-

- lutions", *Bull. Chem. Tehnol. Macedonia*, vol. 18, no. 1, pp. 47-50, 1999.
- [8] M. Jankulovska, L. Šoptrajanova, I. Spirevska, "Behaviour of Glutaconic and Aconitic acid in a sulfuric acid medium", *Bull. Chem. Tehnol. Macedonia*, vol. 25, no. 2, pp. 89-97, 2006.
- [9] J. Reijenga, A. van Hoof, A. van Loon, B. Teunissen, "Development of Methods for the Determination of pKa Values", *Anal. Chem. Insights.*, vol. 8, pp. 53-71, 2013.
- [10] M. J. S. Dewar, K. M. Dieter, "Evaluation of AM1 Calculated Proton Affinities and Deprotonation Enthalpies", *J. Am. Chem. Soc.*, vol. 108, pp. 8075-8086, 1986.
- [11] J. J. P. Stewart, "Optimization of Parameters for Semi-Empirical Methods I-Method", *J. Comput. Chem.*, vol. 10, pp. 209-216, 1989.
- [12] L. P. Hammett, A. J. Deyrup, "A series of simple basic indicators. I. The acidity functions of mixtures of sulfuric and perchloric acids with water", *J. Am. Chem. Soc.*, vol. 54, pp. 2721-2739, 1932.
- [13] J. F. Bunnett, F. P. Olsen, "Linear free energy relationships concerning equilibria in moderately concentrated mineral acids", *Can. J. Chem.*, vol. 44, pp. 1899-1915, 1966.
- [14] K. Yates, R. A. McClelland, "Mechanisms of Ester Hydrolysis in Aqueous Sulfuric Acids", *J. Am. Chem. Soc.*, vol. 89, pp. 2686-2692, 1967.
- [15] R. A. Cox, K. Yates, "Excess Acidities. A Generalized Method for the Determination of Basicities in Aqueous Acid Mixtures", *J. Am. Chem. Soc.*, vol. 100, pp. 3861-3867, 1978.
- [16] G. Stojkovic, E. Popovski, "Determination and structural correlation of pK_{BH}^+ for meta- and para-substituted benzamides in sulfuric acid solutions", *J. Serb. Chem. Soc.*, vol. 71, no. 10, pp. 1061-1071, 2006.
- [17] A. M. Amat, G. Asensio, M. A. Miranda, M. J. Sabater, A. S. Fuentes, "Thermolysis of Unsaturated Dicarboxylic Acids in Sulfuric Acid and Oleum. A Comparison with the CIMS Fragmentation Patterns", *J. Org. Chem.*, vol. 53, pp. 5480-5484, 1988.
- [18] J. W. Larsen, P. A. Bouis, "Protonation of Fumaric and Maleic Acids and Their Diethyl Derivatives", *J. Org. Chem.*, vol. 38, pp. 1415-1417, 1973.
- [19] T. E. Edward, S. C. Wong, "Ionization of Carbonyl Compounds in Sulfuric Acid. Correction for Medium Effects by Characteristic Vector analysis", *J. Am. Chem. Soc.*, vol. 99, pp. 4229-4232, 1977.
- [20] S. Hoshimo, H. Hosoya, S. Magakura, "Ultraviolet, Infrared, and Raman spectra of protonated carboxylic acids", *Can. J. Chem.*, vol. 44, pp. 1961-1965, 1966.
- [21] T. Birchall, R. T. Gillespie, "Nuclear magnetic resonance studies of the protonation of weak bases in fluorosulfuric acid: V Ketones, Carboxylic acids, and some other oxygen bases", *Can. J. Chem.*, vol. 43, pp. 1045-1051, 1965.
- [22] R. Stewart, K. Yates, "The position of Protonation of the Carboxyl Group", *J. Am. Chem. Soc.*, vol. 82, pp. 4059-4061, 1960.
- [23] Z. Geltz, H. Kokocinska, R. I. Zalewski, T. Krygowski, "Thermodynamics of benzoic acid protonation", *J. Chem. Soc. Perkin Trans.*, vol. II, pp. 1069-1070, 1983.
- [24] D. S. Noyse, H. S. Avarbook, W. L. Reed, "Isotope Effects in the Acid-catalyzed Isomerization of Cinnamic Acids", *J. Am. Chem. Soc.*, vol. 84, pp. 1647-1650, 1962.
- [25] G. A. Olah, A. M. White, D. H. O'Brien, "Protonated heteroaliphatic compounds", *Chem. Rev.*, vol. 70, pp. 561-567, 1970.
- [26] F. M. Benoit, A. G. Harison, "Predictive value of Proton Affinity. Ionization Energy Correlations Involving Oxygenated Molecules", *J. Am. Chem. Soc.*, vol. 99, pp. 3980-3984, 1977.
- [27] M. J. S. Dewar, E. G. Zoebisch, E. F. Healy, J. J. P. Stewart, "Development and Use of Quantum Mechanical Molecular Models. 76. AM1: A New General Purpose Quantum Mechanical Model", *J. Am. Chem. Soc.*, vol. 107, pp. 3902-3909, 1985.
- [28] HyperChem(TM) Professional 7.51, Hypercube, Inc., 1115 NW 4th Street, Gainesville, Florida 32601, USA
- [29] M. A. Poul, F. A. Long, " H_0 and related indicator acidity functions", *Chem. Rev.*, vol. 57, pp. 1-45, 1957.
- [30] K. Yates, J. B. Stevans, A. R. Katritzky, "The ionization behaviour of amides in concentrated sulphuric acids", *Can. J. Chem.*, vol. 42, p. 1957-1970, 1964.
- [31] K. Yates, H. Wai, G. Welch, R. A. McClelland, "Medium Dependence of Acidity Functions and Activity Coefficients in Perchloric Acid", *J. Am. Chem. Soc.*, vol. 95, pp. 418-426, 1973.
- [32] N. Perišić-Janjić, D. Baćanović, M. Lazarević, J. Janjić, "Protonation of N-[1-(benzotriazole-1-yl) methyl] benzamide derivatives and N¹-(phenylaminomethyl) benzotriazole derivatives", *Bull. Chem. Tehnol. Macedonia*, vol. 13, pp. 91-95, 1994.
- [33] D. P. Bajkin, N. U. Perišić-Janjić, "Spectrophotometric study of the protonation of some benzilomoxime derivatives", *J. Serb. Chem. Soc.*, vol. 61, pp. 17-22, 1996.
- [34] A. Bagno, B. Bujnicki, S. Bertrand, C. Comuzzi, F. Dorigo, P. Janvier, G. Scorrano, "Site of protonation of carboxylic and non-carboxylic amides in the gas phase and in water", *Chem. Eur. J.*, vol. 5, pp. 523-536, 1999.
- [35] C. T. Davis, T. A. Geissman, "Basic Dissociation Constants of Some Substituted Flavones", *J. Am. Chem. Soc.*, vol. 76, pp. 3507-3511, 1954.