

BEHAVIOUR OF GLUTACONIC AND ACONITIC ACID IN A SULFURIC ACID MEDIUM

Milena S. Jankulovska, Lidija Šoptrajanova, Pinka Spirevska

*Institute of Chemistry, Faculty of Sciences and Mathematics, Sts Cyril and Methodius University,
PO Box 162, MK-1001 Skopje, Republic of Macedonia
jankulovska2003@hotmail.com*

The behaviour of glutaconic and aconitic acids in a sulfuric acid medium [$c(\text{H}_2\text{SO}_4) = 1.000 \text{ mol/dm}^3$ to 17.000 mol/dm^3] was studied by ultraviolet and visible spectroscopy. The influence of the solvent on the appearance of the registered spectra was compensated by the use of the characteristic-vector analysis (CVA). It was concluded that at the employed sulfuric acid concentrations glutaconic acid is protonated whereas in the case of aconitic acid the protonation reaction is followed, at higher sulfuric acid concentrations, by formation of the corresponding anhydride. Discussed here are the possible sites where the protonation may take place, taking into account the values of the partial charges calculated according to the AM1 semiempirical method. The values of the dissociation constants of glutaconic acid were calculated by the application of the Hammett's equation, using several acidity functions. The thermodynamic constants of protonation and the solvation parameters m , m^* and ϕ were estimated using the Yates–McClelland, the "excess acidity", and the Bunnett–Olsen methods.

Key words: aconitic acid; glutaconic acid; protonation; ultraviolet spectroscopy

ОДНЕСУВАЊЕ НА ГЛУТАКОНСКАТА И АКОНИТНАТА КИСЕЛИНА ВО СУЛФУРНА КИСЕЛИНА

Применувајќи ги методите на ултравиолетовата и видлива спектроскопија, следено е однесувањето на глутаконската и аконитната киселина во средина на сулфурна киселина ($c(\text{H}_2\text{SO}_4) = 1.000 \text{ mol/dm}^3$ до 17.000 mol/dm^3). Влијанието на растворувачот врз изгледот на регистрираните спектри е компензирано со употреба на методот на карактеристична векторска анализа (СВА). Заклучено е дека при користените концентрации на сулфурна киселина доаѓа до протонирање на глутаконската киселина, додека кај аконитната киселина при повисоки концентрации на сулфурната киселина реакцијата на протонирање е следена и со реакција на формирање соодветен анхидрид. Беа дискутирани и можните места на кои доаѓа до протонирање на киселините, при што се земени предвид и вредностите на парцијалните полнежи пресметани според семиемпирискиот AM1 метод. Вредностите на константите на дисоцијација на протонираната форма на глутаконската киселина беа пресметани со примена на Hammett-овата равенка, со употреба на повеќе киселински функции. Термодинамичките константи на протонирање и солватационите параметри m , m^* и ϕ беа пресметани според методите на Yates–McClelland, вишок на киселост и методот на Bunnett–Olsen.

Клучни зборови: аконитна киселина; глутаконска киселина; протонирање; ултравиолетова спектроскопија.

INTRODUCTION

The protonation process of some carboxylic acids (maleic, fumaric, acrylic, metacrylic, citraconic, mesaconic and itaconic) in strong acids (H_2SO_4 , HClO_4 , HCl , H_3PO_4 and oleum) has been

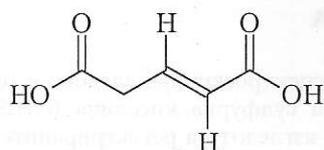
studied spectrophotometrically by several authors [1–4]. In the spectra the medium effects usually contribute to the bathochromic or hypsochromic shift of the absorption bands. To compensate for this medium effect, various methods have been employed such as the principal-component analy-

sis (PCA) [5], the target-testing method of factor analysis [6, 7] and characteristic-vector analysis (CVA) [8].

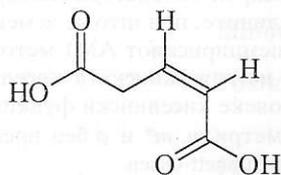
The values of the dissociation constants of the protonated forms of the acids and the solvation parameters m , ϕ and m^* were determined by the methods of Yates and McClelland [9], Bunnett, and Olsen [10] and by the "excess acidity" function method [11]. The dissociation constants of the protonated forms of the investigated acids (pK_{BH^+}) were also graphically determined using the methods of Poul and Long [12], Bonner [13], and Yates and McClelland [9]. The thermodynamic protonation constants (pK_{app}) were determined with the method of Seyda [14]. It should be pointed out that the values of these constants (and those of the solvation parameters) are important, especially for understanding the mechanism of the reactions in which the investigated acids take part.

Thus, the purpose of our work was to follow the protonation process of glutaconic (2-pentenedioic acid) and aconitic (1-propene-1,2,3-tricarboxylic acid) in sulfuric acid media, and to determine the dissociation constants of the protonated forms, the solvation parameters m , ϕ and m^* , and the thermodynamic protonation constants of the investigated acids.

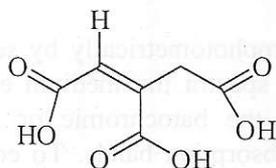
Both acids, as it is already well known, exist in their *cis* and *trans* forms:



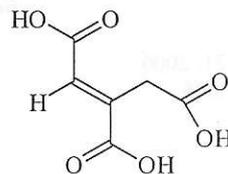
cis-glutaconic acid



trans-glutaconic acid



cis-aconitic acid (*E*)



trans-aconitic acid (*Z*)

In aqueous solutions these two acids undergo isomerization and are transformed into the more stable *trans*-form [15].

EXPERIMENTAL

Solutions and measurement

Two series of solutions with the concentration of the investigated acids $c_{\text{glutaconic acid}} = 1.09 \cdot 10^{-4}$ mol/dm³ and $c_{\text{aconitic acid}} = 1.01 \cdot 10^{-4}$ mol/dm³ were prepared. The concentration of the investigated acids was constant, while the concentration of sulfuric acid varied from 1 mol/dm³ to 17 mol/dm³. The ultraviolet spectra of the two series of solutions were recorded (with 1 nm resolution) at room temperature in the wavelength region from 190 to 360 nm on a Varian Cary 50 spectrophotometer in a 1 cm quartz cell. The UV spectra were recorded 24 hours after the preparation of the solutions (the solutions were stable during that time period).

In order to obtain more precise data for the concentration of the protonated (BH^+) and the unprotonated (B) forms of glutaconic acid, the absorbance values were measured at four selected wavelengths: 200, 206, 218 and 226 nm.

To determine the molar absorption coefficient of the unprotonated form of glutaconic acid at selected wavelengths, the absorbance values were measured when the sulfuric acid concentration was 1 mol/dm³, while for the molar absorption coefficient values of the protonated form of the acid the absorbance values were measured when the sulfuric acid concentration was 17 mol/dm³.

The two carboxylic acids (glutaconic and aconitic) and sulfuric acid were of analytical grade p.a. (Merck and Alkaloid, Skopje). The stock solutions of glutaconic and aconitic acid were prepared with redistilled water as primary standards. The concentration of the sulfuric acid was determined by titration with a standard solution of sodium hydroxide.

Calculations

The pK_{BH^+} values of glutamic acid were calculated using the Hammett [16] equation:

$$pK_{BH^+} = H_0 + \log(c_{BH^+}/c_B) \quad (1)$$

in which H_0 is the Hammett acidity function, c_{BH^+} is the concentration of the protonated form of the acid, and c_B is the concentration of the unprotonated form of the acid. The ratio between the concentrations of the protonated and the unprotonated forms of the acids is known as *ionization ratio*, I . The values of the H_0 were taken from the literature [12, 13, 16–19], while the ionization ratio values were calculated from spectrophotometric data according to the Beer's law [20–22]. In order to minimize the influences of random errors, an overdetermined system of four equations with two unknown parameters was set up.

For a quantitative characterization of glutamic acid, the acidity constants were calculated using several methods mentioned in the introduction. The values of the slopes obtained by different methods, the correlation coefficients and the standard deviation values were calculated as well. These calculations were made using the Microsoft Excel computer program.

To compensate for the effect of the medium, the characteristic-vector analysis (CVA) [8] was employed. In addition, the computer program of Edward and Wong [23] was used.

RESULTS AND DISCUSSION

The behaviour of the acids

The ultraviolet spectra of the series of glutamic and aconitic acid solutions are shown in Fig. 1 and Fig. 2, respectively.

Predictably, identical spectra were obtained irrespective on whether the solutions of the *cis* or of the *trans* form of the acids were used. As previously mentioned, in aqueous solutions the *cis* forms of both acids are transformed into the more stable *trans* forms, *i.e.* that isomerization processes take place [15].

As it can be seen in Fig. 1 and Fig. 2, a single absorption band resulting from the $\pi \rightarrow \pi^*$ electron transitions (denoted 1 in Fig. 1 and Fig. 2) exists in the spectrum of each of the two investigated acids (found around 206 nm for glutamic

acid and around 226 nm for aconitic acid). On increasing the sulfuric acid concentration, the absorption bands shift from 206 nm to 226 nm in the spectra of glutamic acid and from 226 nm to 206 nm in the spectra of aconitic acid and, simultaneously, the intensity of the bands increases.

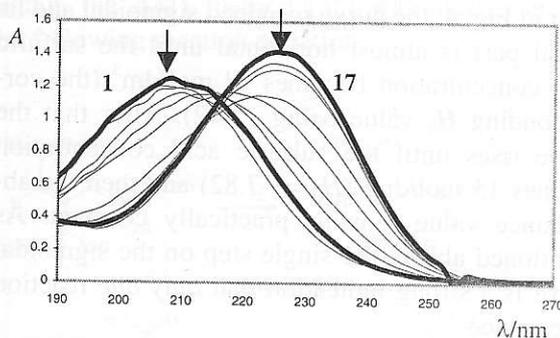


Fig. 1. Ultraviolet spectra of glutamic acid ($c = 1.09 \cdot 10^{-4}$ mol/dm³) in sulfuric acid media (from $c = 1$ mol/dm³, spectrum 1, to $c = 17$ mol/dm³, spectrum 17)

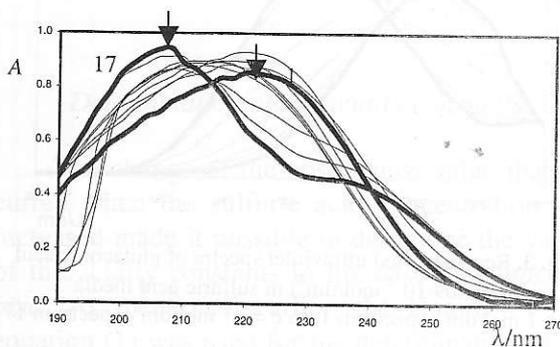


Fig. 2. Ultraviolet spectra of aconitic acid ($c = 1.01 \cdot 10^{-4}$ mol/dm³) in sulfuric acid media (from $c = 1$ mol/dm³, spectrum 1, to $c = 17$ mol/dm³, spectrum 17)

On a careful examination of the spectra, the monotonic change in the *glutamic acid* spectra becomes obvious. Namely, the band is continuously bathochromically shifted until it reaches the final position at sulfuric acid concentration of 17 mol/dm³ (denoted by 17 in Fig. 1). At the same time its intensity is also changed but no new band appears. We expected, on the basis of our previous studies and also of those of other authors [1–4], that an isobestic point would appear between 210 nm and 220 nm, but it does not manifest itself clearly and with an exact position. The reason is, almost certainly, the effect of the solvent [24], which was confirmed after the application of the characteristic-vector analysis (CVA) which reconstructed the spectra. As it is plainly visible in Fig. 3, an isobestic point is present at 214 nm. This indicates that a single reaction is taking place in the studied solutions and, consequently, only two mo-

lecular species capable of absorbing the electromagnetic radiation are present in them.

Such a conclusion is additionally supported by the appearance of the $A_{226} = f[c(\text{H}_2\text{SO}_4)]$ curve. If a single reaction takes place, the curve would be sigmoidal with only one step on it. As it can be seen in Fig. 4, the curve is indeed sigmoidal and its initial part is almost horizontal until the sulfuric acid concentration becomes 11 mol/dm^3 (the corresponding H_0 value being -5.42). After that the curve rises until the sulfuric acid concentration reaches 15 mol/dm^3 ($H_0 = -7.82$) and then the absorbance value remains practically constant. As mentioned above, the single step on the sigmoidal curve is a strong indication that *only one* reaction takes place.

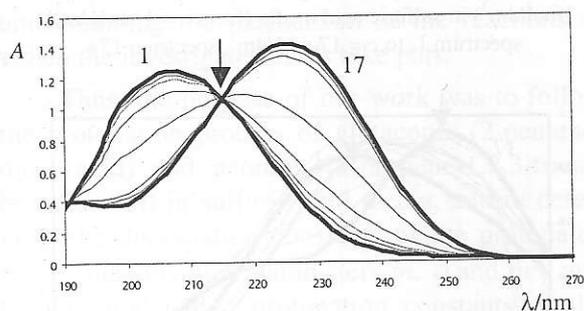


Fig. 3. Reconstructed ultraviolet spectra of glutamic acid ($c = 1.09 \cdot 10^{-4} \text{ mol/dm}^3$) in sulfuric acid media (from 1 mol/dm^3 , spectrum 1, to $c = 17 \text{ mol/dm}^3$, spectrum 17)

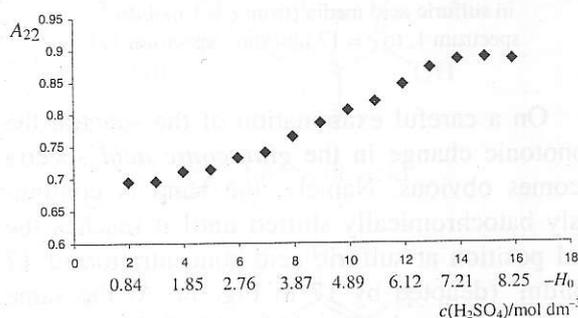
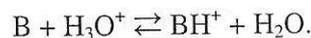


Fig. 4. Absorbance values ($\lambda = 226 \text{ nm}$) for glutamic acid as a function of the sulfuric acid concentration

Based on what was already mentioned, and having in mind some other studies [1–4, 25, 26, 27] performed on acids with a similar structure (citraconic, mesaconic, itaconic, fumaric and maleic), we concluded that the most probable candidate for such a reaction is the *protonation* of glutamic acid (which, in this case, behaves as a Brønsted base) and that the general equation of such a reaction would be

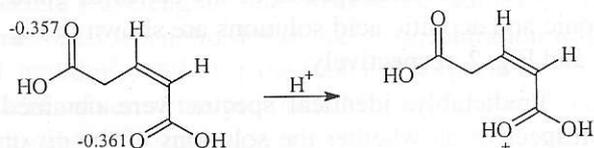


However, in order to make it applicable to a given reaction only, the exact position of the site at which the protonation takes place must be determined.

Pospíšil and his collaborators [25] were among the first to study the protonation, in strongly acidic media, of some unsaturated dicarboxylic acids (fumaric and maleic) applying the methods of UV and NMR spectroscopy. They showed that protonated molecules are indeed present and stated that the protonation takes place not only at the carbonyl oxygens in the carboxylic groups, but also at the double bonds (similar conclusions were earlier reached by Noyse et al. [27]). On the other hand, Olah and co-workers [28] suggested that only the carbonyl group is protonated and this was later confirmed by the detailed studies of Larsen and Bouis and of Benoit and Harrison [26, 29] who found that the affinity for the protons of the singly bonded oxygens in the carboxylic acids and esters is for $0.8 - 1.1 \text{ eV}$ lower than that of the carbonyl oxygens of these same compounds.

The subsequent studies of a number of authors [30–33] who employed UV, IR, Raman and NMR spectroscopy proved that the protonation indeed takes place on the carbonyl group. Identical were the conclusions of Geltz et al. [34] who followed the protonation of benzoic acid using the methods of mass spectrometry.

According to all mentioned studies (especially the more recent ones) and the partial charges (calculated with the semiempirical AM1 quantum chemical method [35]) the equation for the protonation of glutamic acid would be:



The situation in the case of *aconitic acid* is different (Fig. 2). The only clearly observable spectral band shifts towards shorter wavelengths and, which is even more important, it is not monotonic (in addition to the hypsochromic shift, a bathochromic shift is observed in a few cases of solutions with a lower sulfuric acid concentrations).

It is important to note that, besides the main peak, a weak band is also present in the spectrum.

On increasing the acidity (by replacing sulfuric acid with oleum) the intensity of the additional band increases. Contrary to that, on dilution of the solution with water (i.e. on decreasing the sulfuric acid concentration) the band disappears.

The variation of the absorbance at 236 nm by changing the acidity (Fig. 5) indicates that more than one reaction is taking place in solution. Namely, the inspection of Fig. 5 shows that more than one step exists on the curve. The conclusion is further strengthened by Fig. 2 where an isobestic point seems to be present around 190 nm although the wavelength is low to allow a definite conclusion.

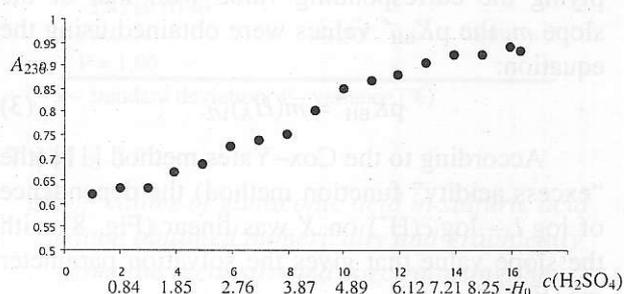


Fig. 5. Absorbance values ($\lambda = 236$ nm) for aconitic acid as a function of the sulfuric acid concentration

The literature data on the formation of anhydrides of organic carboxylic acids even at low concentrations of mineral acids [25, 26, 33], as well as our previous results on the behaviour of citraconic acid in oleum [1], suggest that not only the protonation of the acid, but also cyclization, leading to the formation of the aconitic acid anhydride, is taking place.

In the reconstructed spectra of aconitic acid (shown in Fig. 6) the isobestic point around 220 nm is clearly visible, whereas the intensity of the second band (which suggests the presence of the aconitic acid anhydride) is appreciably lowered.

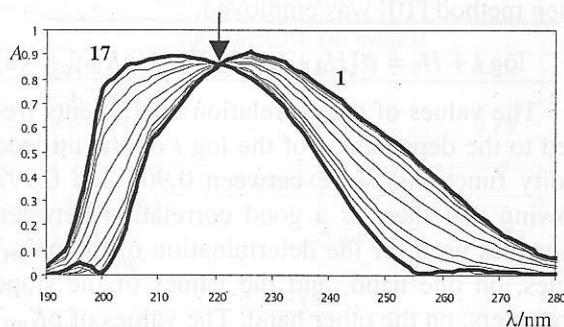
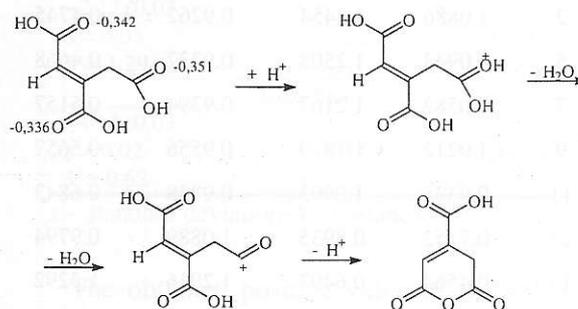


Fig. 6. Reconstructed ultraviolet spectra of aconitic acid ($c = 1.01 \cdot 10^{-4}$ mol/dm³) in sulfuric acid media (from $c = 1$ mol/dm³, spectrum 1, to $c = 17$ mol/dm³, spectrum 17)

This shows that, at the sulfuric acid concentrations employed ($1 - 17$ mol dm⁻³) the reaction of formation of protonated acid is predominant, rather than that of formation of the corresponding anhydride.

The calculated values of the partial charges (again, the AM1 method [35] was used) suggest the following reaction equation:



Determination of the acidity constants

The change of the absorbance value that occurred when the sulfuric acid concentration was increased made it possible to determine the values of the acidity constants in the case of *glutaconic acid*. As mentioned earlier, the Hammett's [16] equation (1) was used for the determination of the pK_{BH^+} values of various acids but, to the best of our knowledge, there are no literature data for the acidity functions when carboxylic acids are used as indicators. Thus, the pK_{BH^+} values were calculated using other acidity functions (the amide function H_A [17,18], the function of Poul and Long [12] and that of Bonner [13]) obtained for compounds with the same protonation center as in the carboxylic acids. We determined the values of $\log I$ for glutaconic acid using the spectrophotometric data obtained at four selected wavelengths. These values are given in Table 1.

The dependence of $\log I$ on H_A is shown in Fig. 7. As it can be seen, the slope parameter m is not equal to unity, because the solvation of the protonated glutaconic acid is different from the solvation which occurs when indicator bases are used for the determination of the acidity functions. The best slope (the value closest to unity) was obtained with the amide acidity function and this is why this function was considered to be the most adequate one.

Table 1

Data obtained by the spectrophotometric measurement of glutaconic acid solutions ($c = 1.09 \cdot 10^{-4} \text{ mol/dm}^3$) in sulfuric acid media (from $c = 1 \text{ mol/dm}^3$ to $c = 17 \text{ mol/dm}^3$)

| $c(\text{H}_2\text{SO}_4)$ mol/dm ³ | A_{200} (99.46; 38.72)* | A_{206} (113.8; 56.55)* | A_{218} (84.68; 111.2)* | A_{226} (43.45; 125.6)* |
|---|------------------------------|------------------------------|------------------------------|------------------------------|
| 1 | 1.0881 | 1.2449 | 0.9264 | 0.4753 |
| 2 | 1.0886 | 1.2454 | 0.9262 | 0.4745 |
| 5 | 1.0943 | 1.2508 | 0.9237 | 0.4668 |
| 7 | 1.0582 | 1.2167 | 0.9394 | 0.5157 |
| 9 | 1.0212 | 1.1819 | 0.9556 | 0.5657 |
| 11 | 0.9335 | 1.0993 | 0.9938 | 0.6843 |
| 13 | 0.7152 | 0.8935 | 1.0889 | 0.9794 |
| 15 | 0.4564 | 0.6497 | 1.2016 | 1.3292 |
| 16 | 0.3911 | 0.5882 | 1.2301 | 1.4176 |
| 17 | 0.4235 | 0.6186 | 1.2159 | 1.3737 |

*Molar absorption coefficient values ($\epsilon \cdot 10^3/\text{mol}^{-1}\text{dm}^2$) of the unprotonated and the protonated form

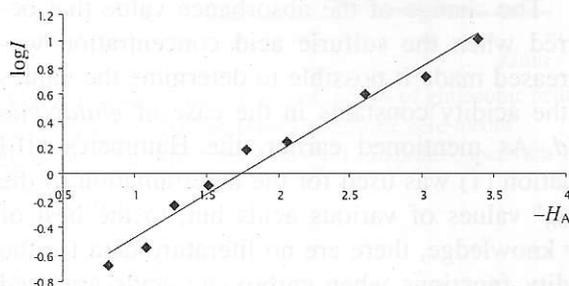


Fig. 7. Dependence of the ionization ratio, $I = c_{\text{BH}^+}/c_{\text{B}}$, of glutaconic acid ($c = 1.01 \cdot 10^{-4} \text{ mol/dm}^3$) on the amide acidity function (H_A)

The $\text{p}K_{\text{BH}^+}$ values, graphically obtained values [$(H_X)_{1/2}$], and the slope values for different acidity functions are presented in Tables 2–5.

When a given acidity function was used, the $\text{p}K_{\text{BH}^+}$ values obtained numerically and graphically are similar (see Tables 2–5). Also, there are no significant differences between the $\text{p}K_{\text{BH}^+}$ values calculated from the experimental and the reconstructed spectra. This could be seen from the values of the standard deviation and variance presented in Tables 2–5. This is an indication that the differences came from the influence of the solvent *i.e.* from the solvation process of the molecules of the carboxylic acids.

The thermodynamic $\text{p}K_{\text{BH}^+}$ values and the values of the solvation parameters m , ϕ and m^* were calculated using the Yates–McClelland [9], Bunnett–Olsen [10] and Cox–Yates [11] methods, respectively.

The calculations according to the method of Yates and McClelland [9] were made on the basis of the equation

$$\log I = -m H_A + \text{p}K_{\text{BH}^+} \quad (2)$$

when the values of the slope m were close to 1.

It is assumed that the acid is half-protonated when $\log I = 0$, *i.e.* when $H_A = (H_A)_{1/2}$. By multiplying the corresponding value with that of the slope m , the $\text{p}K_{\text{BH}^+}$ values were obtained using the equation:

$$\text{p}K_{\text{BH}^+} = m(H_A)_{1/2} \quad (3)$$

According to the Cox–Yates method [11] (the “excess acidity” function method) the dependence of $\log I - \log c(\text{H}^+)$ on X was linear (Fig. 8) with the slope value that gives the solvation parameter m^* (Eqn. 4)

$$\log I - \log c(\text{H}^+) = m^* \cdot X + \text{p}K_{\text{BH}^+} \quad (4)$$

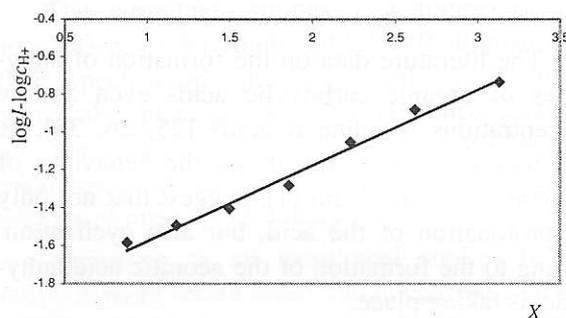


Fig. 8. Dependence of $\log I - \log c_{\text{H}^+}$ on X for glutaconic acid ($c = 1.01 \cdot 10^{-4} \text{ mol/dm}^3$) in sulfuric acid media (from $c = 1 \text{ mol/dm}^3$ to $c = 17 \text{ mol/dm}^3$)

Equation (5) was used when the Bunnett and Olsen method [10] was employed.

$$\log I + H_0 = \phi [H_0 + \log c(\text{H}^+)] + \text{p}K_{\text{BH}^+} \quad (5)$$

The values of the correlation coefficients (related to the dependence of the $\log I$ on the utilized acidity functions) were between 0.907 and 0.999 showing that there is a good correlation between the values used for the determination of the $\text{p}K_{\text{BH}^+}$ values, on one hand, and the values of the slope parameters, on the other hand. The values of $\text{p}K_{\text{BH}^+}$ obtained using different methods were close to one another, especially when the data obtained from the reconstructed spectra were used.

Table 2

pK_{BH^+} values of glutamic acid in sulfuric acid medium obtained numerically and graphically from the experimental spectra, using the Hammett's equation

| H_0 -Poul and Long method | | |
|-----------------------------|---------------|-------|
| pK | $(H_0)_{1/2}$ | Slope |
| -4.01 ± 0.04 | | |
| $s = 0.04$ | -4.08 | 0.68 |
| $V = 0.97$ | | |
| H_0 -Bonner | | |
| -3.62 ± 0.04 | | |
| $s = 0.05$ | -3.64 | 0.72 |
| $V = 1.31$ | | |
| H_A | | |
| -3.47 ± 0.0140 | | |
| $s = 0.04$ | -3.50 | 0.99 |
| $V = 1.06$ | | |

* s - standard deviation, V - variance (%)

Table 3

pK_{BH^+} values of glutamic acid in sulfuric acid medium obtained numerically and graphically from the reconstructed spectra, using the Hammett's equation

| H_0 -Poul and Long method | | |
|-----------------------------|---------------|-------|
| pK | $(H_0)_{1/2}$ | Slope |
| -4.36 ± 0.03 | | |
| $s = 0.02$ | -4.40 | 0.70 |
| $V = 0.44$ | | |
| H_0 -Bonner | | |
| -3.79 ± 0.03 | | |
| $s = 0.03$ | -3.82 | 0.75 |
| $V = 0.73$ | | |
| H_A | | |
| -3.64 ± 0.01 | | |
| $s = 0.02$ | -3.66 | 1.03 |
| $V = 0.69$ | | |

* s - standard deviation, V - variance (%)

Table 4

Thermodynamic pK_{BH^+} values of glutamic acid in a sulfuric acid medium, calculated from the experimental spectra

| Yates-McClelland method | | |
|-------------------------|---------------|-------|
| pK | $(H_0)_{1/2}$ | slope |
| -4.27 ± 0.04 | | |
| $s = 0.04$ | -4.32 | 0.75 |
| $V = 0.87$ | | |
| Bunnet-Olsen | | |
| -2.45 ± 0.02 | | |
| $s = 0.02$ | -2.44 | 0.76 |
| $V = 0.78$ | | |
| Cox-Yates | | |
| -4.09 ± 0.03 | | |
| $s = 0.02$ | -4.14 | 0.63 |
| $V = 0.57$ | | |

* s - standard deviation, V - variance (%)

Table 5

Thermodynamic pK_{BH^+} values of glutamic acid in sulfuric acid medium, calculated from the reconstructed spectra

| Yates-McClelland method | | |
|-------------------------|---------------|-------|
| pK | $(H_0)_{1/2}$ | Slope |
| -4.24 ± 0.06 | | |
| $s = 0.05$ | -4.34 | 0.74 |
| $V = 1.28$ | | |
| Bunnet-Olsen | | |
| -2.17 ± 0.03 | | |
| $s = 0.03$ | -2.23 | 0.78 |
| $V = 1.29$ | | |
| Cox-Yates | | |
| -4.14 ± 0.03 | | |
| $s = 0.02$ | -4.07 | 0.63 |
| $V = 0.62$ | | |

* s - standard deviation, V - variance (%)

The obtained positive value of the solvation parameter ϕ indicate that the solvation in the case of glutamic acid is more pronounced than the solvation in the case of the Hammett's indicators used in the setting up the H_0 scale [36].

The thermodynamic protonation constant K_{app} , was determined using the method of Seyda [14]. According to this author, the basicity was defined as the protonation ratio I of the standard solvent (an acid with a concentration of 1 mol/dm³) at room temperature and normal pressure. Using the method of Seyda, the calculations were made with the equation (6):

$$-\log I = pK_{app} - (n + 1) \log c(\text{HA}). \quad (6)$$

If $c(\text{HA}) = 1 \text{ mol/dm}^3$, then $-\log I = pK_{app}$. It can be easily seen that pK_{app} is the intercept of the straight line of the form

$$\log I = f[-(n + 1) \log c(\text{HA})].$$

According to Seyda, $-(n + 1) \log c(\text{HA})$ is the best acidity function for a given base in acid media which completely satisfied the Hammett's postulate (the slope of the linear dependence of $\log I$ on H_X being equal to 1). The value of the thermodynamic protonation constants of glutamic acid calculated by the method of Seyda [14] is 8.34.

CONCLUSIONS

The protonation process of glutamic acid and aconitic acid occurs in sulfuric acid media, *i.e.* both investigated acids behave as weak oxygen bases. During the protonation reaction the gluta-

conic acid is transformed into its protonated form. Aconitic acid is also protonated but this reaction is followed by partial formation of the corresponding anhydride. This is the reason why the quantitative characterization of the protonation reaction is possible only for glutaconic acid.

The protonation process of glutaconic acid begins at a sulfuric acid concentration of about 11 mol/dm³ ($H_0 = -5.42$) and is completed at sulfuric acid concentration above 15 mol/dm³ ($H_0 = -7.82$).

The numerically obtained pK_{BH}^+ values are not significantly different from the graphically obtained ones if the same acidity function is used. The pK_{BH}^+ values obtained from the experimental and the reconstructed spectra are in a good agreement. The small differences that appear are a result of the influence of the medium.

The values of the standard deviation are lower when the amide acidity function was used. Hence, this approach best describes the protonation process, in agreement with the previous findings [1–4, 17, 18].

The values of the standard deviation obtained from the reconstructed spectra are lower than those obtained from the experimental spectra, but the differences are statistically insignificant.

By comparing the results for m^* , ϕ and pK_{BH}^+ in the case of glutaconic acid with those for acids of similar type (such as mesaconic and itaconic acid [1]), it is easy to see that in all studied cases a correlation exists between the values of m^* , ϕ and pK_{BH}^+ ; the higher the value of m^* is, the more negative the pK_{BH}^+ values get. This means that if the solvation process is less favored, the basicity is lower as well [36, 37]. On the other hand, positive values of ϕ correspond to higher values of pK_{BH}^+ and the basicity of glutaconic acid is higher. Thus, the basicity can be expressed using either the pK_{BH}^+ values or the solvation parameters m and ϕ .

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ОПРЕДЕЛЕНИЕ КОНСТАНТ НА ДИСОЦИАЦИЯ НА НЕКОИ
НОВОСИНТЕЗИРАНИ СУБСТИТУИРАНИ 2,4-ТРИАЗОЛИН-3-ТИОНИ
ВО СРЕДИНА НА НАТРИУМ ХИДРОКСИД

Во овие студии се определени константите на дисоцијација на некои новосинтезирани субституирани 2,4-триазолин-3-тиони во водна средина. Концентрациите на киселините се определени со помош на спектрофотометрија, а концентрациите на нивните соодветни форми се определени со помош на титриметрија. Константите на дисоцијација се определени со помош на методот на карактеристичен вектор. Резултатите се споредени со литературните податоци.

Во овие студии се определени константите на дисоцијација на некои новосинтезирани субституирани 2,4-триазолин-3-тиони во водна средина. Концентрациите на киселините се определени со помош на спектрофотометрија, а концентрациите на нивните соодветни форми се определени со помош на титриметрија. Константите на дисоцијација се определени со помош на методот на карактеристичен вектор. Резултатите се споредени со литературните податоци.