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DETERMINATION OF THE pK VALUES OF GLUTACONIC ACID IN SULFURIC ACID MEDIUM

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Introduction

The unsaturated dicarboxylic acids are easily polymerised and used in the manufacture of polymers. As a result, their behaviour in various reaction media has been studied by many authors. In spite of this, the studies of the behaviour of glutaconic acid are scarce. In our previous work [1–3] ultraviolet spectroscopy was used as a convenient method for the study of the protonation of various types of compounds which can undergo such reactions. Extending our work, we now report the results of the investigation of the protonation of the glutaconic acid in sulfuric media in an attempt to determine the pK value of the acid.

Experimental

Series of solutions in which the concentration of glutaconic acid was constant ($1.094 \cdot 10^{-4}$ mol/L) and that of sulfuric acid was varied from 1.0 mol/L to 16.5 mol/L were prepared. The UV spectrum of each solution was recorded between 190 nm and 290 nm on a Hewlett-Packard 8452A Diode Array Spectrophotometer. The absorbance values needed for the calculations were determined at four selected wavelengths: 200 nm, 206 nm, 218 nm and 226 nm. At these wavelengths, the values of the molar absorption coefficients of the protonated and non-protonated form of the glutaconic acid were determined. For that purpose the solutions of the acid with the highest concentration of sulfuric acid (16.5 mol/L) and the solution of the acid with the lowest sulfuric acid concentration (1.0 mol/L), respectively, were used.

All employed chemicals were reagent grade Merck products.

Results and Discussion

General Investigation

In the ultraviolet (UV) spectra of glutaconic acid in aqueous sulfuric acid medium (see Fig. 1, curve 1) a band with a maximum around 206 nm appears. When the concentration of sulfuric acid increases, this absorption band gradually shifts towards longer wavelengths (curves 2–10) reaching the value of 226 nm (Fig. 1, curve 10). In the series of spectra, an isobestic point located around 214 nm seems to appear. In an attempt to determine the true position of the isobestic point, the initially obtained spectrophotometric data (A , \square) were subjected to a computer analysis using the *characteristic vector analysis* (CVA) program [4] for the compensation of medium effects. The reconstructed spectra are shown in Fig. 2 where a clear isobestic point, located at 214 nm is easily seen.

The spectral changes described above show that a chemical change is taking place. The appearance of the isobestic point suggests that only two absorbing species exist in the solution. That means that there is only one step of reaction between glutaconic acid and sulfuric acid, leading to formation of protonated glutaconic acid. The existence of only one step on the sigmoidal curve $A_{\square} = f(c_{\text{sulph.ac.}})$, given in Fig. 3, shows that only one of the carboxylic group is protonated.

* Editorial note: Recognized by Greece as FYROM.

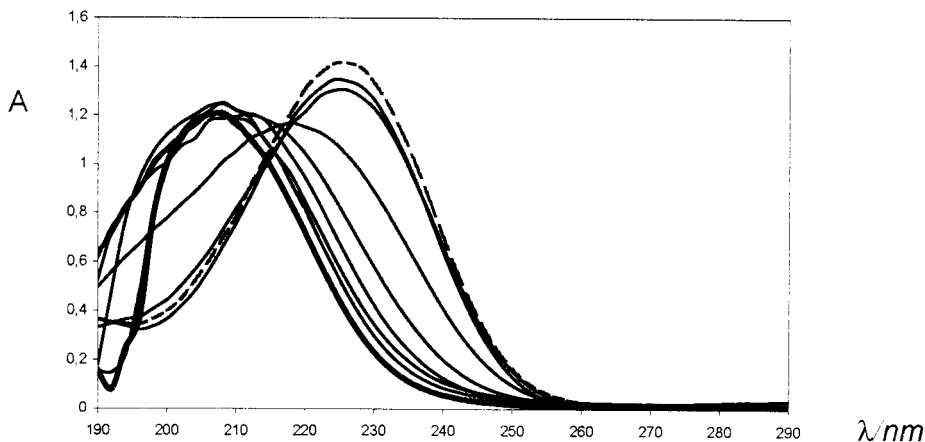


Figure 1. Ultraviolet spectra (from 1 to 10) of glutamic acid ($1.094 \cdot 10^{-4}$ mol/L) in sulfuric acid (from 1.0 mol/L to 16.5 mol/L).

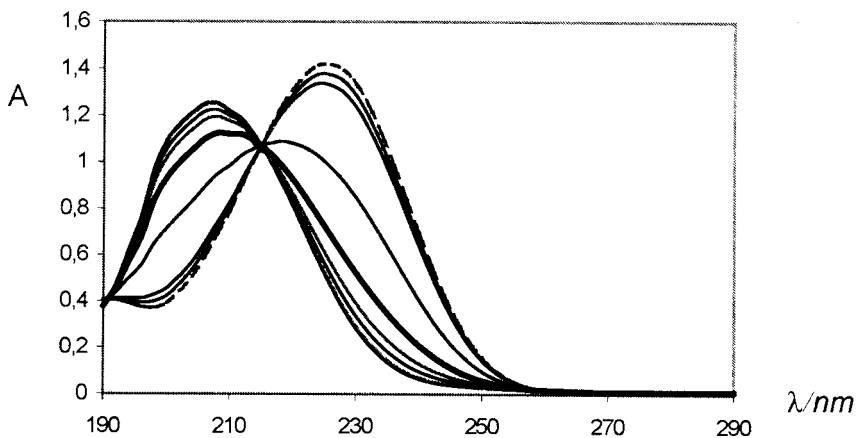


Figure 2. Reconstructed ultraviolet spectra (from 1 to 10) of glutamic acid ($1.094 \cdot 10^{-4}$ mol/L) in sulfuric acid (from 1.0 mol/L to 16.5 mol/L).

Apparently, the sulfuric acid strength is not sufficiently high to ensure the protonation of the second carboxylic group as well.

Determination of the pK Value

The knowledge of pK values is important for studying and understanding the mechanisms of the reactions, which take place in acidic media.

In the present work, the reconstructed spectral curves were used to estimate the pK value of glutamic acid in sulfuric acid as a proton-donor. The Hammett's equation [5]

$$pK_{BH^+} = H_0 + \log I$$

where H_0 is the acid (Hammett's) function and l is the ratio of the equilibrium concentrations of the protonated acid (BH^+) and its non-protonated (BH) form was used in the course of the calculations.

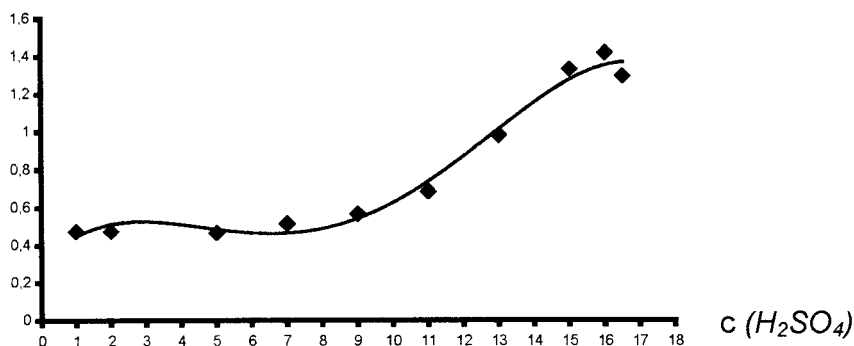


Figure 3. The absorbance values (at $\lambda=226$ nm) as a function of the sulfuric acid concentration.

Using the Beer's law, from the absorbance data at the four selected wavelengths and the molar absorption coefficients (see Table 1), an over-determined system of four equations with two unknowns (c_{BH^+} and c_{BH}) was obtained and was solved with the MATHCAD software package [6]. MATHCAD was also used to calculate the pK_{BH^+} value (6,4068).

Table 1. The data obtained by spectrophotometric measurement of glutaconic acid ($c = 1.094 \times 10^{-4}$ mol/L) in sulfuric acid solution.

$c(H_2SO_4)$ mol dm^{-3}	A_{200} (99458; 21832)*	A_{206} (113797; 56553)*	A_{218} (84685; 111149)*	A_{226} (43447; 125574)*
1	1.08808	1.24493	0.92645	0.47531
2	1.08863	1.24546	0.92621	0.47456
5	1.09434	1.25084	0.92373	0.46684
7	1.05821	1.21679	0.93947	0.51569
9	1.02118	1.18190	0.95560	0.56575
11	0.93350	1.09927	0.99379	0.68429
13	0.71520	0.89355	1.08891	0.97944
15	0.45648	0.64974	1.20162	1.32923
16	0.39113	0.58815	1.23009	1.41759
16.5	0.42353	0.61869	1.21597	1.29378

*The values in parentheses are the molar absorption coefficient ($\bar{\epsilon} \text{ mol}^{-1} \text{ dm}^2$) of nonprotonated and protonated acid, respectively.

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