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Protonation of maleic and fumaric acid in aqueous sulfuric acid solutions

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The protonations of maleic and fumaric acid in an acidic medium (aqueous solutions of sulfuric acid) were followed spectrophotometrically at room temperature. The acid-base equilibria were characterised qualitatively and quantitatively. The pK_{BH^+} values were determined using the Hammett equation, employing several acid functions in order to determine which of them describes best the protonation process of the studied organic acids. The thermodynamic pK_{BH^+} values as well as those of the solvation parameters *m*, *m** and ϕ and of the thermodynamic protonation constants (or, rather, the $pK_{a,p}$ values) were also defermined. The method of characteristic vector analysis (CVA) was used to reconstruct the experimental spectra.

Keywords: maleic acid, fumaric acid, protonation, spectrophotometry.

INTRODUCTION

Maleic and fumaric acid are important industrial substances which have a broad range of practical application. They are used in the production of synthetic resins, agricultural preparations and drugs, as additives for the removal of impurities and hymidity from organic solvents and oil fuels,[1] as bleaching additives in detergents,[2] *etc*. As a result of this, their behaviour in various reaction media has been studied by many authors. Thus, Das and co-workers[3] studied the acid-base equilibria of maleic and fumaric acid in water and determined their dissociation constants while Simon and co-workers[4] investigated these acids in mixtures of organic solvents and water. Later, Pospišil *et al*.,[5] while polarographically studying the mechanisms of reduction of maleic and fumaric acid in acidic media (aqueous sulfuric acid), registered two polarographic waves, the first of which (a positive one) originates from the reduction of the protonated molecules of the acids, AH_3^+. The presence of the protonated forms was established by UV[5] and, later,[6] by NMR spectroscopy. The above-mentioned authors determined the dissociation constants of the protonated maleic and fumaric acids, using the Hammett equation[7] and the values

of the molar absorption coefficient (ε), wave length of the absorption maximum (λ_{max}), and the half-width (*S*) of the band. The p*K* values are 8.4 and 7.6 for maleic acid, and 18.4, 21.3 and 20.1 for fumaric acid.[5]

Later, Larsen and Bouis[8] studied the protonation of these two unsaturated carboxylic acids in the superacids FSO_3H and FSO_3H-SbF_5 and found that the protonation takes place on the carbonyl oxygen. This conclusion was confirmed by Benoit and Harrison.[9] Normaly, these authors found that the proton affinity of the singly bonded carboxylic oxygen is by 0.8 – 1.1 eV lower than the proton affinity of the doubly bonded one. More recently, Amat *et al.*[10] studied the protonation of maleic and fumaric acid in 96 % H_2SO_4 and in oleum (with 63 % SO_3) and identified *o*-protonated forms in the NMR spectra.

In previous studies,[11] we quantitatively and qualitatively characterised the acid-base equilibria of maleic and fumaric acid in $HClO_4$, H_2SO_4–C_2H_5OH and oleum. In the present paper, the results of a study of the reaction of these two geometric isomers in aqueous solutions of H_2SO_4 are reported. These studies complement the previous ones and are intended to contribute to the clarification of the mechanisms of the reactions which take place in acidic media. It should, perhaps, be pointed out that in strongly acidic media the studied organic acids behave as *bases* and that this is the origin of the notation B and BH^+ (used in the text which follows).

The protonation reactions of the two presently studied organic acids were characterised quantitatively by calculating their dissociation constants (or, rather, the pK_{BH^+} values). The calculations were performed using the Hammett equations and three acid functions (the function of Paul and Long,[12] that of Bonner[13] and the amide function[14]). The most appropriate of them was, then, used to calculate the thermodynamic dissociation constant according to the method of Yates-McClelland.[15] When calculating the pK_{BH^+} values, the methods of Bunnett-Olsen[16] and Cox-Yates[17] were also applied and the solvation parameters m^* and ϕ were determined. Finally, the thermodynamic constants of protonation (the $pK_{a,p}$ values) were estimated using the method of Seyda.[18]

EXPERIMENTAL

Two series of solutions in which the concentration of maleic and fumaric acid was constant (1×10^{-4} mol/dm^3) and that of sulfuric acid was varied (from 1 mol/dm^3 to 17.5 mol/dm^3) were prepared. The behaviour of the dicarboxylic acids was monitored through the changes in the 190–250 nm region of the absorption spectra recorded on a Hewlett Packard 8452 A Diode-Array Spectrophotometer. A sulfuric acid solution (of the same concentration as in each investigated solution) was used as a blank. The absorbance values needed for the calculations were determined at four selected wavelengths: 212, 216, 222 and 228 nm (for maleic acid) and 202, 210, 222 and 228 nm (for fumaric acid). At these wavelengths (using Bear's law) the values of the molar absorption coefficients of the protonated and non-protonated form of the carboxyl acids were determined. For this, solutions in which the concentrations of the organic acids were 0.8×10^{-4} mol/dm^3; 1×10^{-4} mol/dm^3 and 1.2×10^{-4} mol/dm^3, while the H_2SO_4 concentration was kept constant (1 mol/dm^3 for the non-protonated form and 17.5 mol/dm^3 for the protonated one) were prepared and the absorbance values (at the mentioned four wavelengths) for each of them were recorded. The data for the values of the molar absorption coefficients and the absorbance values for each investigated solution, substituted into the Beer law, resulted in an

overdetermined system of equations with two unknowns: the concentrations of the unprotonated and that of the protonated acid. This system was solved with the MATHCAD software package. MATHCAD was also used to calculate the Hammett pK_{BH^+} values for three acid functions, those of Poul and Long,[12] of Bonner[13] and the amide function[14] in order to see which of them would best describe the protonation of the studied organic acids.

The pK_{BH^+} value was graphically estimated by the method of Davis and Geissman,[19] Yates-McClelland,[15] Bunnett-Olsen[16] and the „excess of acidity" method,[17] using the STATGRAPH softwere package, which was also used to calculate the $pK_{a,p}$ values by the method of Seyda.[18] Simultaneously, the slopes of the straight lines $\log I = f(H_A)$; $\log I + \log c(H^+) = f(X)$; $\log I + H_0 = f[H_0 + \log c(H^+)]$ and $\log I = f[-(n + 1) \log \bar{c}(HA)]$ were determined. Also the correlation coefficients and the standard deviations were calculated. In the above equations and in the following, X (the „excess acidity") is the difference between the observed acidity and that which the system would have if it were ideal, I is the protonation ratio (the ratio of the equilibrium concentrations of the protonated and non-protonated forms of the base, *i.e.*, of the BH^+ and B species, respectively) and $c(J)$ is the *relative* equilibrium concentration of species J, *i.e.*, the ratio of the equilibrium concentration and the standard value of the concentration taken as 1 mol dm^{-3}.

To compenstate for the effecxt of the medium on the appearance of the spectra, the method of characteristic vector analysis (CVA)[20] was employed using the computer programme of Edward and Wong.[21]

The two organic acids (maleic and fumaric) and sulfuric acid were p.a. products obtained from Merck and Alkaloid (Skopje). Stock solutions of maleic and fumaric acid (in both cases the acid concentration was 5×10^{-3} mol/dm^3) were prepared as primary standards, whereas the exact concentration of sulfuric acid was determined by titration with a standard NaOH solution.

RESULTS AND DISCUSSION

General

The UV spectra of maleic and fumaric acid in aqueous solutions of H_2SO_4, recorded under identical experimental conditions are shown in Figs. 1 and 2, respectively. It is easy to see that the absorption bands of these two unsaturated carboxylic acids (with maxima at 205 nm for maleic and 210 nm for fumaric acid) shift towards longer wavelengths as the sulfuric acid concentration increases, apparently as a result of the protonation of the acids. This is in agreement with the findings of Pospišil *et al.*,[5] Amat *et al.*[10] and our own for the case of some other dicarboxylic acids in H_2SO_4.[22–24] It should be noted that there is a slight difference in the position of the absorption bands in the spectra of the two acids. Thus, at a sulfuric acid concentration of 17.5 mol/dm^3, the absorption maximum is at 222 nm in the spectrum of maleic acid and at 220 nm in that of fumaric acid.

The spectral changes caused by the changes in the sulfuric acid concentration are better seen from the plot of absorbance (at $\lambda = 228$ nm) *vs.* H_2SO_4 concentration (Fig. 3). The initial parts of both curves (up to a sulfuric acid concentration of ≈ 6 mol/dm^3 for fumaric acid and up to a H_2SO_4 concentration of ≈ 3 mol/dm^3 for maleic acid) are almost horizontal. Such a difference in the spectral behaviour is probably due to differences in the effect of the medium in the two cases, in agreement with the conclusions by Johnson *et al.*[25]

Then, a noticeable change in the absorbance with increasing mineral acid concentration (in other words, the extent of the protonation reaction) occurs, for both ac-

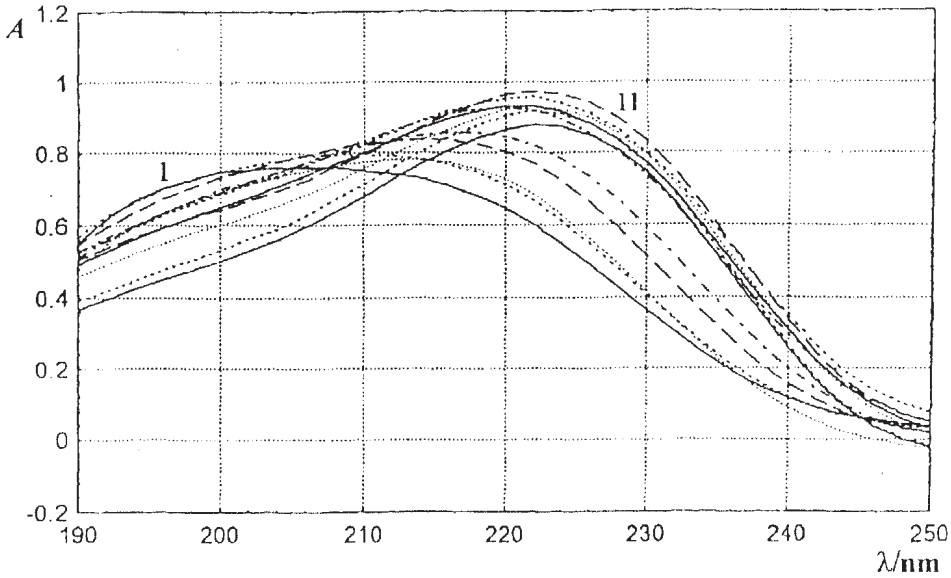

Fig. 1. Ultraviolet spectra (from 1 to 11) of maleic acid (c = 1.0 ×10^{-4} mol dm^{-3}) in sulfuric acid (from c = 1.0 mol dm^{-3} to c = 17.5 mol dm^{-3}).

ids, up to a sulfuric acid concentration of ≈ 15 mol/dm^3, whereas both curves exhibit an upper plateau at higher concentrations of the mineral acid. Obviously, at c(H_2SO_4) > 15 mol/dm^3 both maleic and fumaric acid exist in their protonated form.

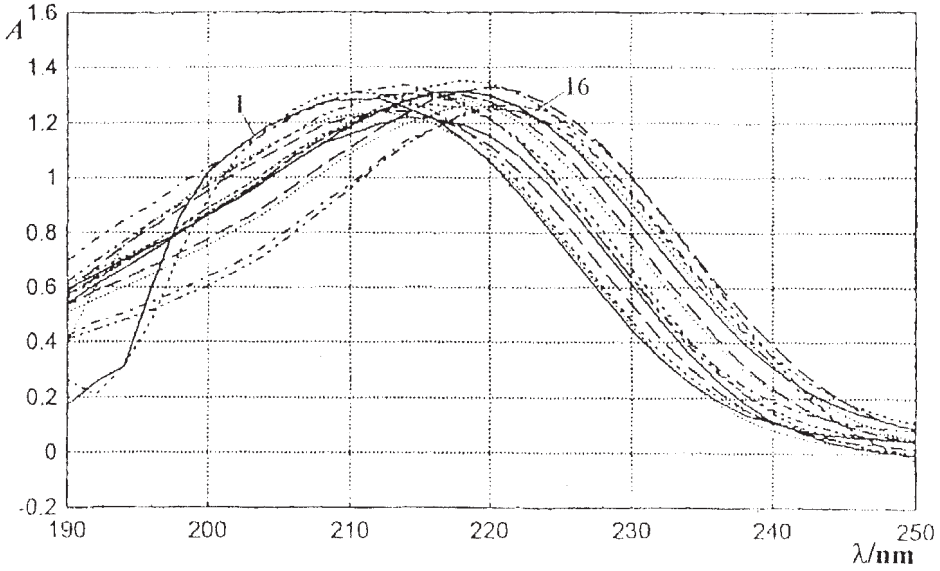

Fig. 2. Ultraviolet spectra (from 1 to 16) of fumaric acid (c = 1.0×10^{-4} mol dm^{-3}) in sulfuric acid (from c = 1.0 mol dm^{-3} to c = 17.5 mol dm^{-3}).

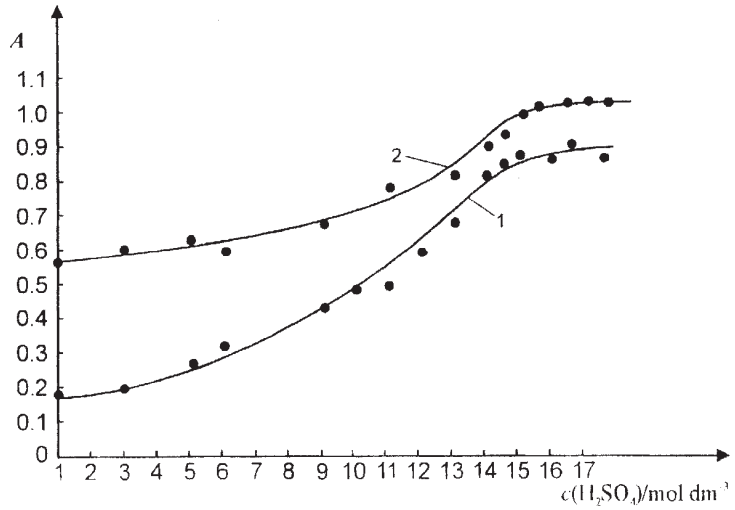

Fig. 3. The absorbance values (at λ = 228 nm) as a function of the sulfuric acid concentration, for maleic acid 1) and for fumaric acid 2).

The existence of only one step on the sigmoidal curve (Fig. 3) suggests that only one of the carboxylic groups is protonated. If this is indeed the case, then only two absorbing species would be present and all spectral curves should pass through one common (isobestic) point. As seen from Figs. 1 and 2, this is obviously not the case, as was observed for other similar systems studied earlier.[20,21,23] The studies have, namely, shown that the effect of the medium causes a slight lateral shift of the absorption bands, which results in the absence of an isobestic point. However, by

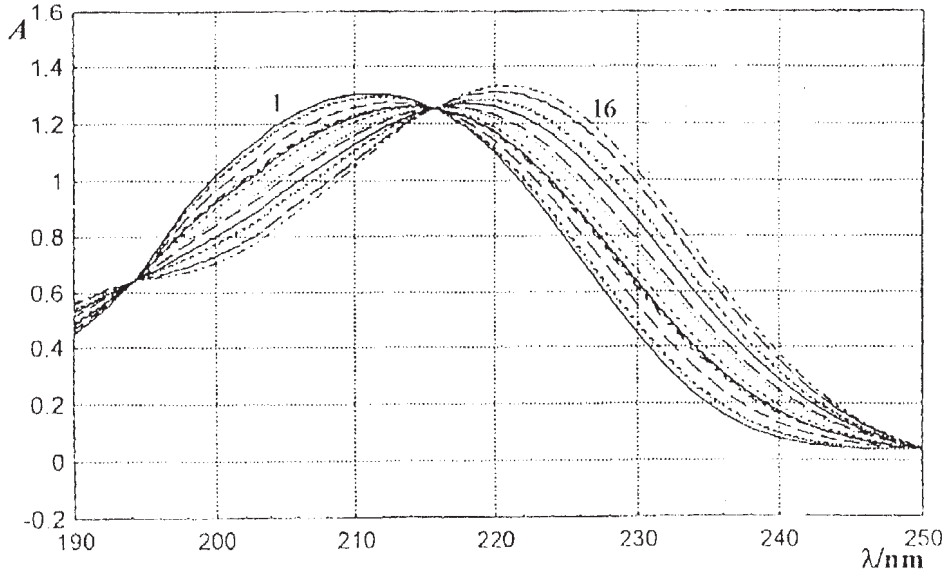

Fig. 4. Reconstructed ultaviolet spectra (from 1 to 11) of maleic acid ($c = 1.0 \times 10^{-4}$ mol dm^{-3}) in sulfuric acid (from c = 1.0 mol dm^{-3} to c = 17.5 mol dm^{-3}).

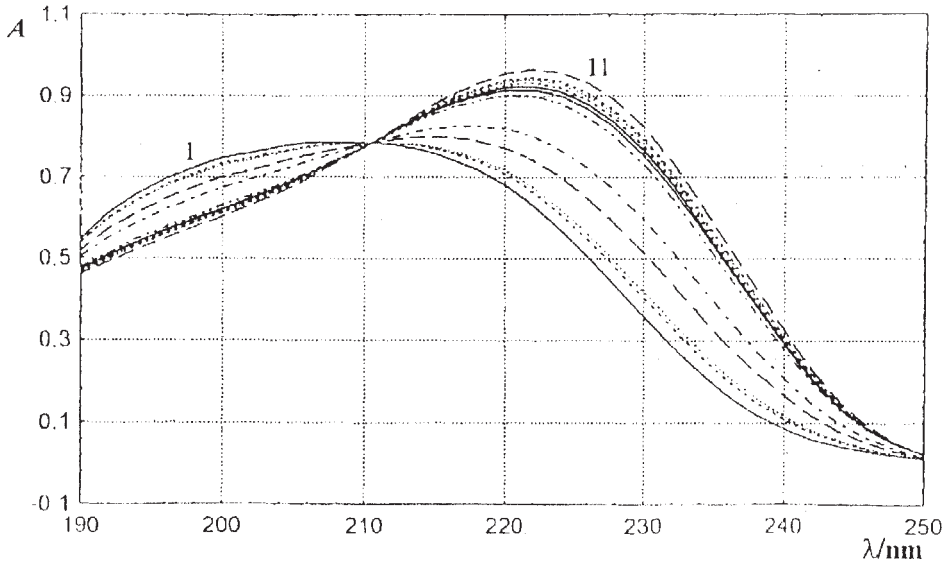

Fig. 5. Reconstructed ultaviolet spectra (from 1 to 11) of maleic acid ($c = 1.0\times10^{-4}$ mol dm^{-3}) in sulfuric acid (from $c = 1.0$ mol dm^{-3} to $c = 17.5$ mol dm^{-3}).

application of characteristic vector analysis,[20] reconstructed spectra were obtained (Figs. 4 and 5) in which clear isobestic points are present. These spectra were then used to obtain the data needed to calculate the thermodynamic acid constants, pK_{BH^+} and the solvation parameters m,[15] m^*,[17] and ϕ.[16]

Determination of the p*K values*

Knowledge of pK_{BH^+} values is important for studying and understanding the mechanisms of the reactions which take place in acidic media. Hence, the pK_{BH^+} values for maleic and fumaric acids were estimated using several methods. In general, the pK_{BH^+} values were determined using the Hammett equation (1):

$$pK_{BH^+} = H_0 + \log I \quad (1)$$

where H_0 is the acid function and I is the ratio of the equilibrium concentrations of the protonated acid and its non-protonated form (calculated as explained in the Experimental section).

Obviously, in order to calculate the pK_{BH^+} values, data for the acid function and for the ratio I are needed. The concentrations necessary for estimating the value of I, calculated from the absorbance values determined at four wavelengths for each sulfuric acid concentration, for maleic and fumaric acid are given in Table I and II, respectively.

The main problem in the calculation of pK_{BH^+} values using the Hammett equation is related to the nature of the acid function which best describes the protonation of the studied carboxylic acids. In absence of relevant acid functions defined for carboxylic acids as indicators, functions determined for compounds in which the same basic centre (the carbonyl oxygen) is protonated were used. Two

such functions were tested – the amide function[14] and the Bonner acid function.[13] For comparison, the original Hammett function (with slight changes suggested by Poul and Long[12]) was also employed.

The numerically ("pK") and graphically [$(H_X)_{1/2}$] obtained constants and the slopes of the log $I = f(H_X)$ straight lines are given in Table III. As can be seen, they are in good agreement with each other but there is a noticeable disagreement with the values found in the literature.[5] It should be noticed, however, that the literature data are old and obtained when inferior experimental and computational techniques were used.

TABLE I. The data obtained by spectrophotometric measurement of maleic acid (c = 1.0×10^{-4} mol dm^{-3}) in sulfuric acid solutions

$c(H_2SO_4)$ mol dm^{-3}	A_{212} (46927; 76815)*	A_{216} (35328; 85185)*	A_{222} (26281;91993)*	A_{228} (17095; 84000)*
1	0.4737	0.3772	0.2641	0.1722
5	0.6096	0.5268	0.4075	0.2841
9	0.7411	0.7062	0.6023	0.4287
10	0.7920	0.7657	0.6668	0.4795
11	0.7806	0.7731	0.6839	0.4912
12	0.8331	0.8375	0.7649	0.5926
13	0.8369	0.8581	0.8221	0.6678
14	0.8630	0.9094	0.9194	0.8013
14.5	0.8360	0.8975	0.9314	0.8343
15	0.8574	0.9187	0.9571	0.8638
16	0.7944	0.8671	0.9295	0.8533
16.5	0.8336	0.9101	0.9737	0.8958
17	0.7238	0.8088	0.8797	0.8078
17.5	0.7575	0.8453	0.9156	0.8381

*The values in parentheses are the molar absorption coefficients (ε/mol^{-1} dm^2) of nonprotonated and protonated acid, respectively

From the data in Table III, it is obvious that, due to the different degree of solvation of the two studied acids at a given acidity, the slopes are not equal to unity. The investigated acids, namely, do not behave in the same way as the indicator bases used to define the acid functions.[26]

As can be seen, the best slope value (*i.e.*, the value closest to unity) is obtained when the amide function H_A is used (see Fig. 6). Hence, this function was considered as the most suitable one and used in the Yates-McClelland's equation (see below).

Due to the deviation of the slopes from unity, the estimated "pK" values obtained using all three acid functions in the Hammett equation are *not* thermody-

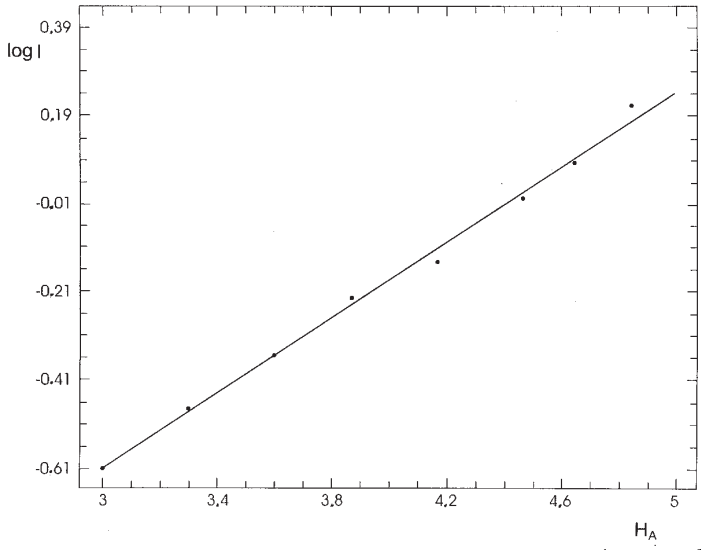

Fig. 6. Dependence of log I on H_A for fumaric acid (c = 1.0 ×10^{-4} mol dm^{-3}).

namic ones.[27] Numerically, they correspond to the H_X values obtained when the acid is half-protonated, *i.e.,* when the concentrations of the non-protonated and protonated acid are equal. According to the obtained results, fumaric acid is half-protonated at sulfuric acid concentrations close to 14 mol/dm^3, whereas the corresponding $c(H_2SO_4)$ value for maleic acid is ≈ 13 mol/dm^3. The data given in Table III show that there is no notable difference between the numerically and graphically obtained values for the constants obtained using a given acid function. Furthermore, there are no large differences between the "pK" values obtained from the experimental and reconstructed spectra.

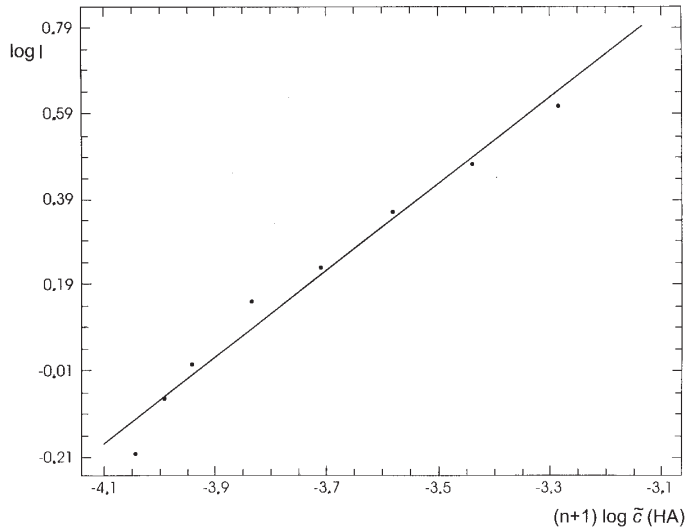

Fig. 7. Dependence of log I on –(n + 1) log $\bar{c}$(HA) for maleic acid (c = 1.0 ×10^{-4} mol dm^{-3}).

TABLE II. The data obtained by spectrophotometric measurement of fumaric acid ($c = 1.0\times10^{-4}$ mol dm^{-3}) in sulfuric acid solutions

$c(H_2SO_4)$ mol dm^{-3}	A_{202} (108737; 63638)*	A_{210} (126658; 92968)*	A_{222} (93602; 122965)*	A_{228} (55935; 108026)*
1	1.1050	1.2810	0.9486	0.5708
3	1.0740	1.3090	0.9856	0.6041
5	1.1300	1.2900	0.9909	0.6165
6	1.0470	1.2310	0.9645	0.5908
9	1.0200	1.2190	1.0260	0.6674
10	1.1000	1.3080	1.1330	0.7719
11	1.0380	1.2630	1.1340	0.7729
12	0.9212	1.1580	1.0790	0.7459
13	0.9531	1.1960	1.1440	0.8095
14	0.9473	1.2080	1.2030	0.8916
14.5	0.9346	1.1960	1.2220	0.9252
15	0.9216	1.1870	1.2590	0.9948
15.5	0.9360	1.2000	1.3040	1.0560
16	0.8124	1.0860	1.2400	1.0200
16.5	0.8342	1.1090	1.3130	1.1140
17	0.6901	0.9775	1.2420	1.0560
17.5	0.6594	0.9613	1.2630	1.1040

*The values in parentheses are the molar absorption coefficients (ε/mol^{-1} dm^2) of nonprotonated and protonated acid, respectively

In order to determine the strength of the studied weak bases (maleic and fumaric acid), the thermodynamic pK_{BH^+} values were calculated using three methods – the method of Yates-McClelland,[15] the method of Bunnet-Owen[16] and that of Cox-Yates.[17] When the Yates-McClelland method was used, in the original equation (2)

$$\log I = -m H_0 + pK_{BH^+} \quad (2)$$

the amide function H_A was used instead of the Hammett acid function H_0. It follows from Eq. (2) that

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

where $(H_A)_{1/2}$ is the value of H_A when $\log I = 0$, *i.e.,* when the concentrations of the non-protonated and protonated acid are equal.

According to the "excess acidity" method, *i.e.,* the Cox-Yates method,[17] the straight lines giving the $\log I - \log c(H^+) = f(X)$ relationships are of the form

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

It follows that the intercept on the ordinate axis is equal to pK_{BH^+}, whereas the slope gives the value of the solvation parameter m^*. The data for X were taken from the literature.[28] The corresponding equation for maleic acid is $\log I - \log \bar{c}(H^+) = 0.30$, *i.e.,* $pK_{BH^+} = -2.62$ and $m^* = 0.30$.

Applying the Bunnett-Olsen's method,[16] the straight line of the form

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

gives an intercept equal to the pK_{BH^+} value and a slope which gives the solvation parameter ϕ. For example, the equation for maleic acid is $\log I + H_0 = 0.81[H_0 + \log c(H^+)] - 2.24$, from which it follows that $\phi = 0.81$ and $pK_{BH^+} = 0.24$.

The results, obtained from both the experimental and reconstructed spectra, are given in Table IV. As can be seen, the values derived by all three methods are not notably different, especially those obtained from the reconstructed spectra.

The values for the parameter m^* are close to the m^* values for amides[28,29] which again proves that the amide function is, of the three studied functions, the most suitable for the studied carboxylic acids.

The values of ϕ obtained in the present work are *positive* as expected for Brønsted bases (such as the investigated carboxylic acids) in which the acid groups are conjugated and sovlation is pronounced.[30]

The data in Table IV show that a correlation exists between the values of m^*, ϕ and pK_{BH^+}. As can be seen, larger positive values for pK_{BH^+} (higher basicity of the given acid) correspond to higher values of ϕ and, correspondingly, to lower values of m^* (which signifies more pronounced solvation[29,31]). In other words, the protonated forms of bases which have a more pronounced interaction with the solvent exhibit a higher basicity, in agreement with the stabilisation of the ions by solvation.[32]

It then follows that the strength of a base may be expressed not only by the pK_{BH^+} values but also by the values of the solvation parameters m^* and ϕ. Our results show that maleic acid (the *cis* isomer) exhibits less pronounced basic properties than its *trans* isomer (fumaric acid) which is to be expected bearing in mind that *trans* carboxylic acids are weaker acids than their *cis* counterparts.[32]

Knowledge of the pK_{BH^+} value does not give complete information about the degree of protonation at a given concentration of the proton donor. In addition to the values of the thermodynamic constants, the values for the slopes (m^* and ϕ), which are measures of the solvation of the cation, are also needed. If all these parameters are known, the degree of protonation in a given acidic solution may be obtained by extrapolation. On the other hand, on the basis of the ϕ parameter (and, analogously, of the parameter m^*), conclusions can be drawn regarding the character (concentrated or dilute) of the strong acid solution which favour protonation. Thus, bases having larger ϕ values are protonated to a higher degree in *dilute* solutions of strong acids and *vice versa*. This is demonstrated by the sigmoidal curves for maleic and fumaric acid shown in Fig. 3. As can be seen (and already discussed), protonation

TABLE III. The values of the dissosiation constants of protonated maleic and fumaric acid in sulfuric acid calculated numericaly and graphically, using the Hammett equation

Acid	The values obtained from the experimental spectra								
	H_0 (Paul and Long method)[12]			H_0 (Bonner method)[13]			H_A (amide method)[14]		
	pK	$(H_0)_{1/2}$	Slope	pK	$(H_0)_{1/2}$	Slope	pK	$(H_A)_{1/2}$	Slope
Maleic	–6.07±0.65	–6.08	0.41	–6.32±0.84	–5.69	0.54	–3.98±0.26	–4.00	0.69
Fumaric	–6.25±0.82	–6.82	0.25	–5.86±0.56	–5.25	0.33	–4.18±0.38	–4.44	0.42
	The values obtained from the reconstructed spectra								
Maleic	–5.44±0.49	–5.22	0.39	–5.22±0.31	–5.26	0.50	–3.63±0.17	–3.66	0.67
Fumaric	–6.24±0.87	–6.69	0.29	–5.86±0.52	–6.15	0.38	–4.17±0.35	–4.36	0.49

TABLE IV. The values of the thermodynamic dissosiation constants of the protonated maleic and fumaric acid in sulfuric acid, calculated from the experimental and reconstructed spectra

Acid	The values obtained from the experimental spectra					
	Yates–McClelland method[15]		Bunnett – Olsen method[16]		Cox – Yates method[17]	
	pK_{BH^+}	m	pK_{BH^+}	ϕ	pK_{BH^+}	m*
Maleic	–2.77±0.13	0.69	–2.93±0.14	0.63	–2.62±0.13	0.30
Fumaric	–1.87±0.02	0.42	–2.24±0.03	0.81	–2.06±0.03	0.16
	The values obtained from the reconstructed spectra					
Maleic	–2.43±0.09	0.67	–2.53±0.09	0.67	–2.30±0.08	0.29
Fumaric	–2.13±0.09	0.49	–2.44±0.10	0.76	–2.08±0.16	0.15

begins at rather low sulfuric acid concentrations (3 mol/dm^3 for maleic and 6 mol/dm^3 for fumaric acid) and is completed at a H_2SO_4 concentration of ≈ 15 mol/dm^3.

To complement the studies discribed above, the basicity of maleic and fumaric acid were estimated by calculating the thermodynamic protonation constant applying the method of Seyda[18] who defined the basicity as the protonation ratio I in a standard solvent (an acid with a concentration of 1 mol/dm^3) at room temperature and normal pressure. The thermodynamic protonation constant p$K_{a,p}$, namely, may be calculated from Eq. (6)

$$I = K_{a,p}\, c(\mathrm{HA})^{n+1} \tag{6}$$

or its logarithmic form (7):

$$-\log I = \mathrm{p}K_{a,p} - (n + 1) \log c(\mathrm{HA}) \tag{7}$$

where the protonation ratio I is the ratio of the concentrations of the non-protonated and protonated forms of the base at a given solvation state, n is the mean value of the solvation distribution (it may be different for different acid-base pairs) and c(HA) is the equilibrium concentration of the strong acid.

It follows that if $\bar{c}(H^+) = 1$, then $-\log I = \mathrm{p}K_{a,p}$ is the intercept of the straight line (see Fig. 7) of the form $\log I = f[-(n + 1) \log c(\mathrm{HA})]$. The results of the described calculations are given in Table V.

According to Seyda,[18] the function $-(n + 1) \log c$(HA) is the best acid function for a given base in a given acidic medium and that it completely satisfies the Hammett postulate that the slope of the line giving the dependence of log I *vs*. H_X should be equal to unity. As seen from Table V, the calculated values for the slopes in the case of the investigated acids are in a complete agreement with this postulate.

TABLE V. The values of the thermodynamic protonation constants of maleic and fumaric acid in sulfuric acid, calculated by applying the method of Seyda[18]

Acid	$n + 1$	p$K_{a,p}$	Slope
Maleic	5.56	6.03±0.17	0.999
Fumaric	3.44	3.92±0.04	0.999

The presented result lead to a conclusion that the order of basicities determined by the values of the thermodynamic protonation constants p$K_{a,p}$ for a standard state defined as a solution of the acid with a concentration of 1 mol/dm^3 is in an agreement with the order derived from the pK_{BH^+} values (the standard state, in this case, is an infinitely dilute solution). This shows the validity of applying both methods for the quantitative characterisation of the protonation equilibria in the case of the investigated acids.

И З В О Д

ПРОТОНИРАЊЕ МАЛЕИНСКЕ И ФУМАРНЕ КИСЕЛИНЕ У ВОДЕНОМ РАСТВОРУ СУМПОРНЕ КИСЕЛИНЕ

КАТИЦА ЈАНКОВСКА, ЛИДИЈА ШОПТРАЈАНОВА и ИЛИНКА СПИРЕВСКА

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Спектрофотометријском методом, на собној температури, праћено је протонирање малеинске и фумарне киселине у киселој средини (водени раствор сумпорне киселине). Дате су и квалитативна и квантитативна карактеристика настале ацидо-базне равнотеже. pK_{BH^+} вредност је израчуната применом Хаметове једначине при чему су коришћене различите киселинске функције да би се утврдило која од њих најбоље карактеризира процес протонирања испитиваних органских киселина. Израчунате су и термодинамичке pK_{BH^+} вредности, вредности солватационих параметар m, m^* и ϕ као и термодинамичке константе протонирања (p$K_{a,p}$ вредности). За реконструкцију експерименталних спектара, примењена је метода карактеристичне векторске анализе (CVA).

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REFERENCES

1. I. Jacson, R. Herman, *Eur. Pat. Appl. EP.* **387** (1990) 219
2. W. D. Robinson, R. A. Mount, Kirk-Othmer, *Encycl. Chim. Technol.,* 3rd ed., M. Grysocu, New York, 1981, p. 14, 770
3. C. Das, U. N. Dach, K. N. Panda, *J. Chem. Soc. Faraday Trans.* **76** (1980) 2152
4. W. Simon, D. Menche, E. Heillbronner, *Helv. Chim. Acta.* **39** (1956) 290
5. L. Pospišil, J. Tomanova, J. Kuta, *Collect. Czech. Chem. Commun.* **33** (1968) 594
6. L. Pospišil, J. Kuta, *Collect. Czech. Chem. Commun.* **34** (1969) 742
7. L. P. Hammett, A. J. Deyrup, *J. Am. Chem. Soc.* **54** (1932) 2721
8. W. Larsen, P. A. Bouis, *J. Org. Chem.* **38** (1973) 1415
9. L. M. Benoit, A. G. Harrison, *J. Am. Chem. Soc.* **99** (1977) 3980
10. A. M. Amat, G. Asensio, M. J. Castello, M. A. Miranda, A. Simon-Fuentes, *Tetrahedron* **43** (1987) 905
11. K. Jankovska, *Ph. D. Thesis*, University of Skopje, 1997, Skopje
12. M. A. Poul, F. A. Long, *Chem. Rev.* **57** (1957) 1
13. T. G. Bonner, J. Philips, *J. Chem. Soc. (B)* (1966) 650
14. K. Yates, J. B. Stevans, A. R. Katritzky, *Can. J. Chem.* **42** (1964) 1957
15. K. Yates, R. A. McClelland, *J. Am. Chem. Soc.* **89** (1967) 2686
16. J. F. Bunnett, F. P. Olsen, *Can. J. Chem.* **44** (1966) 1899
17. R. A. Cox, K. J. Yates, *J. Am. Chem. Soc.* **100** (1978) 3861
18. K. Seyda, *Polish J. Chem.* **57** (1983) 1313
19. C. T. Davis, T. A. Geissman, *J. Am. Chem. Soc.* **76** (1954) 3507
20. R. I. Zalewski, *J. Chem. Soc. Perkin Trans. II* (1979) 1637
21. T. E. Edward, S. C. Wong, *J. Am. Chem. Soc.* **99** (1977) 4229.
22. I. Spirevska, L. Soptrajanova, B. Andonovski, *Glas. Hem. Technol. Macedonia* **8** (1990)151
23. L. Soptrajanova, I. Spirevska, *Glas. Hem. Technol. Macedonia* **10** (1991) 21
24. I. Spirevska, L. Soptrajanova, K. Jankovska, B. Andonovski, *J. Mol. Struct.* **93** (1993) 293

25. C. D. Johnson, A. R. Katritzky, B. J. Ridgewell, N. Shakir, A. M. White, *Tetrahedron* **21** (1965) 1055
26. C. C. Greeg, C. D. Johnson, *J. Am. Chem. Soc.* **90** (1968) 6453
27. E. M. Arnett in Progress in *Physical Organic Chemistry*, Vol. 1, S. G. Cohen, A. Streitwieser and R. W. Taft, Eds. Interscience, New Yoprk, 1963
28. A. Bagno, G. Scorrano, R. A. More O Ferrall, *Rev. Chem. Intermed* **7** (1987) 313
29. V. Lucchini, G. Modena, G. Scorrano, R. A. Cox, K. Yates, *J. Am. Chem. Soc.* **104** (1982) 1958
30. E. M. Arnett in *Proton Transfer Reactions*, E. F. Caldin and V. Gold, Eds., Chapman and Hall, London, 1975
31. A. Levi, G. Modena, G. Scorrano, *J. Am. Chem. Soc.* **96** (1974) 6585
32. M. Lj. Mihailović, *Osnovi teorijske organske hemije i stereo hemije*, Gradjevinska knjiga, Beograd, 1970 (in Serbian).