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POLAROGRAPHIC BEHAVIOUR OF *CIS*- AND *TRANS*-DICARBOXYLIC ACIDS IN PHOSPHATE BUFFER

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The polarographic behaviour of maleic, fumaric, citraconic and mesaconic acids in phosphate buffer of different pH-values and concentrations was investigated. On the basis of these investigations methods for the analysis of maleic and fumaric, or citraconic and mesaconic acids, one in the presence of the other are presented. The phenomenon of the appearance of several waves is explained and the equation of electrode reactions is formulated.

The presence of a double bond, conjugated with acid carbonyl groups makes the *cis*-isomers, maleic and citraconic acids, and the corresponding *trans*-isomers, fumaric and mesaconic acids, polarographically active. The reduction of maleic and fumaric acids at the dropping mercury electrode has been investigated in the strongly acidic medium (HCl), strongly alkaline medium (LiOH) and in buffered media (acetate, ammoniacal, borate and phosphate) at different pH-values[1–17]. The polarographic behaviour of citraconic and mesaconic acids has been investigated to a lesser extent [1,7,15,18,19] mostly in acidic media as well as inacetate phosphate-citrate and borate buffers. All the investigations have shown that the thermodynamically more labile *cis*-configurations of maleic and citraconic acids are being reduced at more positive potentials with respect to the more stable *trans*--configurations of fumaric and mesaconic acids. The purpose of polarographic investigations of these acids has been to find out conditions under which waves of the *cis*- and *trans*-isomers can be sufficiently well separated, so that both isomers can be determined from the same sample, if possible.

Out of several proposition for the simultaneous determination of maleic and fumaric acids [2,13,14,16,17], the best ones proved to be the Warshowsky and Elving procedure[13], which determines maleic and fumaric acids one in the presence of the other, in the ammoniacal buffer at a pH of 8.2. There are only scarce informations about the simultaneous determination of citraconic and mesaconic acids[15,19,20]. In ammoniacal buffer (1 mol dm^{-3}) at pH of 8.1, citraconic acid can be determined with a precision below 3% for concentrations from 0.13 to 0.78 mg cm^{-3} [20], since at pH above 6.5 mesaconic acid does not produce a wave. With respect to the polarographic behaviour of unsaturated acids in the phosphate buffer there are records[16,17] that both maleic and fumaric acids can be determined in this buffer. However, detailed investigations of their polarographic behaviour have not been performed so far. Citraconic acid has been not studied[7], and there are no informations about the polarographic behaviour of mesaconic acid in the

phosphate buffer. Hence, we have studied in this paper the polarographic behaviour of maleic, fumaric, citraconic and mesaconic acids in phosphate buffer, with the purpose to ascertain how the pH-value and the buffer concentration influences the formation of the waves. During the investigations we tried to find out in which ratio of concentrations *cis*- and *trans*-isomers can be determined one in the presence of the other.

EXPERIMENTAL

The polarographic curves wre recorded on a Radiometer Polariter PO4 polarograph. The chart speed was 4 cm min^{-1} (1 mm corresponds to 0.01 V) The sensitivity range from 5 to 200 mA, with damping of oscillation was used.

As indicator electrode the dropping mercury electrode was used. Capillary characteristics were determined in distilled water at a potential of 0 V (with respect to saturated calomel electrode) and with a height of mercury column of 35 cm. Mercury drop time was 4.0 s, while the rate of flow was 2.29 mg s^{-1}. As the reference electrode the saturated calomel electrode was used, The contact between the electrodes was realized by a potassium chloride bridge. The oxygen was being removed from the investigated solution by bubbling purified nitrogen for 8 to 10 min. An inert atmosphere above the solutions during measurements was maintained by flushing with nitrogen. All the measurements were done at 25 ± 0.5°. The height of the recorded waves was measured by means of Müller's graphic method.

Maleic and fumaric acids were of *p.a.* purity, while citraconic and mesaconic were of *purum* grade (Fluka). The purification of the citraconic acid was effected by recrystallization from a mixture of ether and ligroin and of mesaconic acid by recrystallization from water.

The concentration of stock solutions of the investigated acids was 0.05 mol dm^{-3} for maleic and citraconic or 0.025 mol dm^{-3} for fumaric acid, and mesaconic as well. Standardization of the solution was performed by potentiometric titration with the standard solution of sodium hydroxide by using a glass electrode. The acid concentrations in the investigated solutions were from 0.1 to 8.0 mmol dm^{-3}.

Phosphate buffers of the desired pH-values which were used as supporting electrolytes were obtained by neutralization of phosphoric acid of a corresponding concentration by means of a concentrated solution of potassium hydroxide (at least 2 mol dm^{-3}). Thus considerable changes of volume and ionic strength of the solution were avoided. When it was dealt with buffers of concentrations 0.1 and 0.2 mol dm^{-3}, a constant ionic strength was being maintained by adding of potassium chloride (1 mol dm^{-3}).

For maximum suppression freshly prepared 1% gelatine solution was used. Its concentration in the investigated solution was 0.005%.

RESULTS

a. Maleic acid

Maleic acid (2 mmol dm^{-3} for example) gives in a solution which contains 0.1 mol dm^{-3} phosphate buffer and 1 mol dm^{-3} KCl, in the pH-range 1.0—3.0 one well developed cathodic polarographic wave whose height does not vary within the above pH-values, while the half-wave potential shifts from 0.62 to 0.75 V with the increase of pH. The investigation of the type of the limiting current has shown that it is governed by the slow process of diffusion and that the electrode process is irreversible. At a pH of 3.1 there appears another poorly defined, more negative wave ($E_{1/2} = -1.0$). By further increase of pH a height increase of

a more negative wave is obtained on account of the more positive wave (Fig. 1). The total height of both waves is slightly lower (about 2.5%) compared to the height of the waves in the acidic medium. At pH of 4.2 prevails the other, more negative wave, which is diffusion controlled.

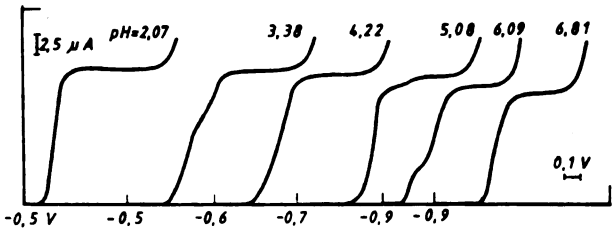

Fig. 1. Polarograms of maleic acid (2 mol dm^{-3}) at different pH-values, in 0.1 mol dm^{-3} phosphate buffer and 1.0 mol dm^{-3} KCl

At pH 3.9 another even more negative wave appears ($E_{1/2} = -1.23$V). This doubling of waves is more distinct compared to the doubling at lower pH--values. The second wave gradually disappears. The investigation at pH 6.09 showed that the wave height does not change by changing the height of the Hg--column, which means that the limiting current is of a kinetic type. Above pH 6.8 only the third wave can be observed whose height is approximately 13% lower than the height of the wave at pH 2.0. This wave is irreversible and meets the criterion for the diffusion current.

If the concentration of phosphate buffer is increased to 0.2 mol dm^{-3}, both doublings of the waves become somewhat less distinct. Already with a concentration of 0.5 mol dm^{-3} of the buffer, the first doubling of the wave can no longer be perceived, while in 1.0 mol dm^{-3} buffer even the second doubling of the wave at pH 5 is hardly noticeable. By increasing the buffer concentration from 0.1 to 1.0 mol dm^{-3}, the pH at which the second doubling of waves appears is increased from 3.1 to 4.5.

On plotting the heights of the waves recorded at constant pH against the acid concentrations, straight line graphs passing through the origin were obtained in all mentioned cases.

b. Fumaric acid

Fumaric acid (2 mmol dm^{-3}, for example) gives in the solution which contains 0.1 mol dm^{-3} phosphate buffer and 1.0 mol dm^{-3} KCl in the pH-range 1.6 to 3.0 one well defined polarographic wave of an approximately equal height within the mentioned pH limits, while the half-wave potential shifts towards more negative values (from — 0.72 V at pH 1.6 to 0.85 V at pH 3.03. The electrode process is irreversible and the limiting current is governed by diffusion. Above pH 3.2 another poorly defined wave can be observed whose height is increased by the increase of the pH value, while the height of the first wave decreases. The total height of both the waves is somewhat lower than the height of the first wave. The limiting current of the second wave is controlled by diffusion, until its height suddenly decreases, after which the limiting current is governed by the rate of the chemical reaction. The electrode process is irreversible. Above pH 3.7 the second more visible doubling of waves can be observed. With the increase of pH values the height of the third wave increases,

while of the second one decreases. Differently from the maleic acid, the third wave of fumaric acid is not so well defined and at pH above 6.5 it coincides with the supporting electrolyte wave.

In case when the phosphate buffer concentration is 1 mol dm^{-3}, the first doubling of the fumaric acid cannot be observed while the second doubling appears only at pH 4.5 (Fig. 2). The second more negative wave is less visible and at pH over 6.65 it coincides with the supporting electrolyte wave. With the increase of pH-values the first wave gradually decreases, especially above pH 4.5, and practically disappears above pH 6.3. The half-wave potential of the wave is considerably shifted towards more negative values with the increase of pH-values: at pH 2.39 it is — 0.75 V, while at pH 5.97 even — 1.185 V. At pH 5.8 the limiting current of the wave has a kinetic character.

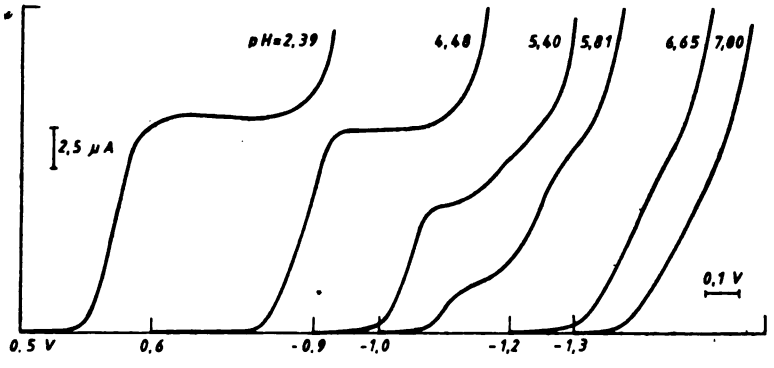

Fig. 2. Polarograms of fumaric acid (2 mmol dm^{-3}) at different pH-values, in 1.0 mol dm^{-3} phosphate buffer

As with maleic acid, with fumaric acid there exists at constant pH-values a linear dependence of the concentration on the wave height also.

The behaviour of maleic and fumaric acids in the presence of sodium or potassium salts of phosphoric acid was studied by using of primary, or secondary sodium or potassium phosphate as supporting electrolytes. With a salt concentration of 1 mol dm^{-3} it was observed that the acids wave height is lower by 2—4% in the presence of sodium salts than in the presence of potassium salts.

c. Mixture of maleic and fumaric acids

The conditions of performing the polarographic analysis of the mixture of maleic and fumarie acids are much more favourable in 1.0 mol dm^{-3} phosphate buffer, since only one wave of each acid apperars at a pH 3.5. In this case the obtained composite wave of both acids is better formed and more suitable for analysis. At pH 3.0 the rate of diffusion governs the height of the limiting current which is of primary interest for analytical purposes. In addition to that, at pH from 2.0 to 3.5 the wave height remains constant. The maleic acid wave at pH 6.6 is diffusion controlled and the height is constant within the pH-range 6—7.

Based on these conclusions we have ascertained the following procedure for polarographic determination of maleic and fumaric acids. The solution which

contains both the acids is recorded in 1.0 mol dm^{-3} phosphate buffer at pH 6.6 and by means of a calibration curve (Fig. 3, curve 2) the concentration of maleic acid is read. Since the height of the maleic acid wave is lower at pH 6.6 than at 3.0, the concentration obtained at pH 6.6 can be used to find the height of the acid at pH 3.0 by using the calibration curve (Fig. 3, curve 1). The obtained value

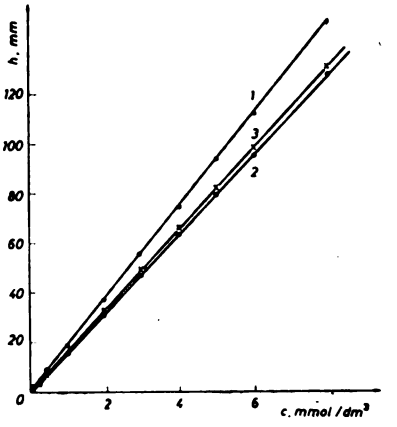

Fig. 3. Dependence of wave height on the concentration of maleic acid at pH 3.0 (*1*) and pH 6.6 (*2*) and fumaric acid at pH 3.0 (*3*), in 1.0 mol dm^{-3} phosphate buffer, 1 mm = 0.4 μA

is subtracted from the total height value of acid waves measured at pH 3.0 and thus we obtain the wave height of fumaric acid at pH 3.0. Then we read from the calibration curve the concentration of fumaric acid which corresponds to this wave height. The relative error for maleic acid is less than 3.7% for concentrations from 0.025 to 0.70 mg cm^{-3}, while for fumaric acid it is below 5% for concentrations from 0.058 to 0.46 mg sm^{-3}, provided the ratio of acid concentrations is not above 1 : 10.

d. Citraconic acid

Citraconic acid (2 mmol dm^{-3}, for example) gives in a solution which contains 0.1 mol dm^{-3} phosphate buffer and 1 mol dm^{-3} KCl up to pH 2.6 one well defined wave whose half-wave potential shifts from − 0.71 to − 0.79 V at pH from 1.27 to 2.6. Above pH 2.6 another wave appears, while above pH 3.5 the third one appears as well. The first wave disappears at pH 4.3, while the second at pH 6.5. The third wave height is constant at pH-values from 6.5 to 7.0 (Fig. 4).

In order to investigate the influence of the buffer concentration on the polarographic behaviour of citraconic acids, measurements were also done in 1.0 mol dm^{-3} phosphate buffer (Fig. 5). In the pH-range from 2.2 to 4.45 another hardly visible wave appears, consisting of two waves. Above pH 4.45 another more negative wave appears, whose height is gradually increased on account of the height of the first more positive wave. The total height of waves in the pH--range where the second wave predominates, is lower for about 10% with respect to the height of wave in the area where the first wave predominates.

In all mentioned cases the process at the electrode is irreversible and the limiting current is governed by diffusion, except in case when the limiting current

of the second wave in 0.1 mol dm^{-3} buffer or the first wave in 1 mol dm^{-3} buffer begins to reduce. In this case it is governed by the rate of the chemical reaction.

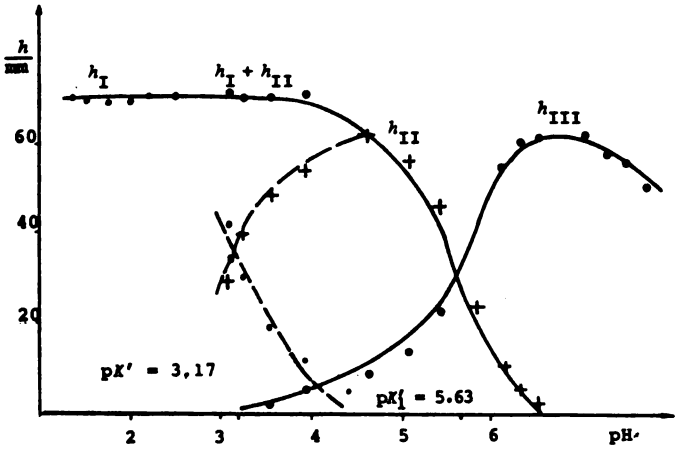

Fig. 4. Dependence of wave heights of citraconic acid (2 mmol dm^{-3}) on pH-value of buffered solution (0.1 mol dm^{-3} phosphate buffer, 1.0 mol dm^{-3} KCl) 1 mm = = 0.2 μA

The investigations have proved that for all the waves there exists a linear dependence of the wave height on the concentration of the acid at constant pH.

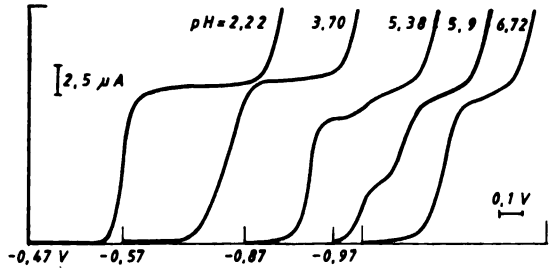

Fig. 5. Polarograms of citraconic acid (2 mmol dm^{-3}) at different pH-values in 1.0 mol dm^{-3} phosphate buffer

e. Mesaconic acid.

Mesaconic acid (2 mmol dm^{-3}, for example) gives one wave in 0.1 mol dm^{-3} phosphate buffer and 1 mol dm^{-3} KCl up to pH 3.1. By increasing the pH-value, another wave can be noticed (Fig. 6). The total height of both the waves is being reduced above pH 3.3 while above pH 4.7 only the second wave remains which practically disappears at pH 6.5. In all the investigated cases it was found that the electrode process is irreversible. The limiting current is governed by diffusion except in the pH-range where the wave height is considerably reduced, and where it is governed by the rate of the chemical reaction.

By increasing the concentration of phosphate buffer to 1 mol dm^{-3} polarograms are obtained as shown in Fig. 7. In the whole investigated pH-range only one polarographic wave appears having an almost permanent height up to pH

4.5. The process at the electrode is irreversible and the limiting current is controlled by the diffusion process. Above pH 4.5 the wave height is reduced and the wave practically disappears at pH 6.8. The investigations of the limiting current

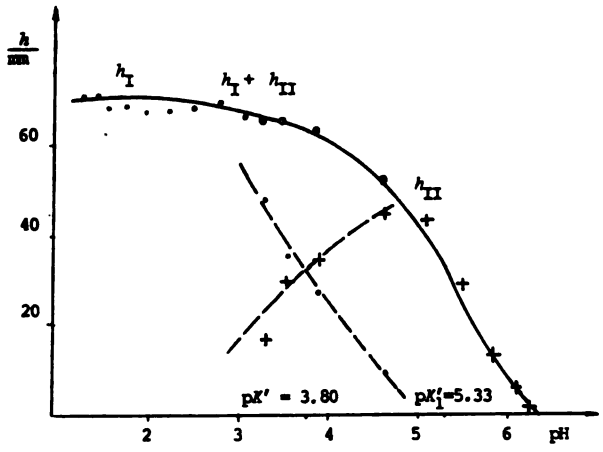

Fig. 6. Dependence of wave heights of mesaconic acid-(2 mmol dm^{-3}) on pH-vad lues of buffered solutions (0.1 mol dm^{-3} phosphate buffer, 1.0 mol dm^{-3} KCl) 1 mm = 0.2 μA

type at pH 5.8 have shown that this is a kinetically controlled process. By reducing the solution acidity, the half-wave potential shifts towards more negative values.

Fig. 7. Polarograms of mesaconic acid (2 mmol dm^{-3}) at different pH-values in 1.0 mol dm^{-3} phosphate buffer

At constant pH it was found that in all the investigated cases there exists a linear dependence of the wave height on the acid concentration.

f. Mixture of citraconic and measconic acids

The investigations of the dependence of half-wave potentials of citraconic and mesaconic acid waves on pH have shown that in 0.1 mol dm^{-3} buffer in the presence of 1.0 mol dm^{-3} an overlapping of at least one wave of both acids occurs due to an insufficient difference of half-wave potentials.

Much more favourable eonditions for the performance of polarographic analysis of both stereoisomess are achieved in 1 mol dm^{-3} phosphate buffer, where the first doubling of citraconic acid waves is hardly visible and where in a wide range of pH-values, mesaconic acid gives only one wave. If for the purpose of determination the waves at pH 3.0 and 6.7 are taken we will be sure that they

are diffusion controlled and that wave heights of citraconic and mesaconic acids do not change with the change of pH per ± 0.5 units.

On the basis of the above discussion we have come to the following sequence for determination of citraconic and mesaconic acids in the solution containing 1 mol dm^{-3} phosphate buffer. First of all, the wave height of the citraconic acid is measured at pH 6.7 and from the calibration curve (Fig. 8, curve 2) the corre-

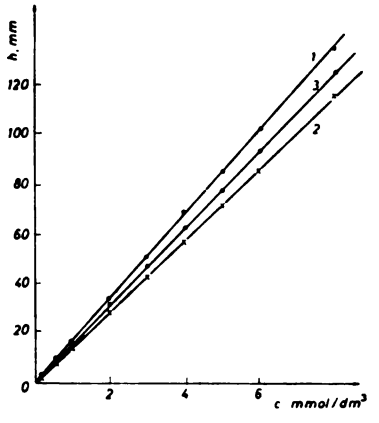

Fig. 8. Dependence of wave height on concentration of citraconic acid at pH 3.0 (*1*) and pH 6.7 (*2*) and mesaconic acid at pH 3.0 (*3*) in 1.0 mol dm^{-3} phosphate buffer) 1 mm = 0.4 μA

sponding concentration) of citraconic acid is read. Further on from the calibraton curve (Fig. 8, curve 1 the height of wave which relates to the concentration of citraconic acid at pH 3.0 is determined. After that, from the height of the wave recorded at pH 3.0 the value is substracted and as a result we obtain the wave height which corresponds to the reduction of mesaconic acid. Finally, we read from the calibration curve the concentration of mesaconic acid which corresponds to this height (Fig. 8, curve 3). The relative error for citraconic acid is less than 2.6%, while for mesaconic less than 5% within the range of acid concentrations from 0.025 to 1.0 mg cm^{-1} and with a ratio 1 : 3 and vice versa. Deviations are greater (above 10%) if the ratio of acid concentrations is higher than 1 : 10.

DISCUSSION

The appearance of several waves in properly buffered medium in the case of maleic and fumaric acids has been explained by Hanuš and Brdička[7], Pospišil and Kuta[9], Koutecky[8] and others, to be the result of reduction of various types of acids on the electrode at various pH-values. Such phenomenon has been found with other organic acids as well[22,23]. It is also well known that due to the fast reaction of recombination with protons of acids present in the solution at certain pH-values, acids which are not present in the solution can also be reduced at the electrode. The mentioned possibility is more pronounced the larger the difference between apparent polarographic dissociation constants and acid dissociation constants. Since the apparent polarographic dissociation constants represent the pH-values with which the height of the more negative wave is equal to the height of the more positive wave[21]:

$$\mathrm{pH} = \mathrm{p}K' + \log\left(I_{\mathrm{neg}}/I_{\mathrm{pos}}\right)$$

they were graphically determined for the investigated acids from the overlapping of curves which represent the dependence of the height of polarographic waves on pH (Figs 4 and 6). The values for the first apparent polarographic dissociation constants (Table I) should be considered as approximate ones being that the first two waves are hardly separated and their heights cannot be always measured with necessary precision. Nevertheless, data from Table I show that there are

TABLE I. Apparent polarographic dissociation constanta, pK', obtained in buffered solutions and dissociation constants, pK (0.1 mol dm^{-3} phosphate buffer, 1.0 mol dm^{-3} KCl)

Acid	p$K(AH_3^+)$	pK'	p$K(AH_2)$	pK_1^3	p$K(AH^-)$	pK_2^3
Maleic	−0.88	3.80	1.945	5.87	6.128	9.00
Fumaric	−1.30	3.90	3.137	5.22	4.619	—
Citraconic	−1	3.17	2.95	5.63	5.98	8.65
Mesaconic	−1	3.80	3.32	5.33	4.73	—

considerable differences between dissociation constants and the apparent polarographic dissociation constants. We have assumed that the dissociation constants of protonized molecules of citraconic and mesaconic acids are of the order of magnitude of the corresponding constants for protonized molecules of maleic and fumaric acids, since the values of the first and second dissociation constants of acids have similar values.

In the pH-range from 2 to 3 only one wave appears for all mentioned acids, except for citraconic acid, whose second wave appears already at pH 2.6. This wave results from the diffusion current. Based on the data on apparent polarographic dissociation constants (Table I) and in accordance with the Pospišil's and Kuta's conclusion[9], we have supposed that the wave obtained in the mentioned pH-range results from reduction of protonized molecules of acids. Since the values of the first dissociation constant of acids are within limits of pK 1.9 to 3.3 (Table I), at the mentioned conditions, the undissociated molecules and monovalent acid ions are present in solution. The processes which are taking place at electrode can be expressed by the following scheme:

$$\begin{array}{ccccc} AH_2 + H^+ & \rightleftharpoons & AH_3^+ & \xrightarrow{2e} & \text{product} \\ & & \updownarrow & & \\ AH^- + 2H^+ & \rightleftharpoons & H^+ + AH_2 & & \end{array}$$

Since it has already been found that reduction at the electrode is irreversible and that the current is controlled by diffusion, the following equation can be applied[24]:

$$dE_{1/2}/dpH = 2.3\,(n - q)\,RT/2\alpha F \qquad (2)$$

where n is the average number of hydrogen atoms of the type which is found in the solution, q — number of hydrogen atoms of the type which is being reduced at the electrode, α the transfer coefficient, R — the universal gas constant (in J K^{-1} mol^{-1}), T — temperature in K and F — the Faraday constant (in C mol^{-1}).

The change of half-wave potentials per unit change which was calculated by means of the mentioned equation and experimentally obtained from the curve slope which represents the dependence $E_{1/2} = f(pH)$ are in good agreement

(Table II). The values of n were calculated at pH 2.5 by means of the dissociation constants of corresponding acids, while α was determined from the slope of the line $\log [(i_d - i)/i] = f(E)$ at pH 2.0. Good agreement between the experimentally ascertained and theoretically calculated slopes $\Delta E_{1/2}/\Delta$ pH is achieved within the pH-range from 1.0 to 2.0 (Table II). Hence we consider that the reduction

TABLE II. Calculated and experimental by obtained values of slope of curves $E_{1/2} = f(pH)$ within a selected pH-range in 0.1 mol dm^{-3} phosphate buffer (in the presense of 1 mol dm^{-3} KCl)

Acid	pH range	n	α	$\Delta E_{1/2}/\Delta$pH	
				Theoretical	Experimental
Maleic	1—2	1.76	0.66	55	55
	2—3	1.22	0.74	71	80
	7—8	0	0.40	74	75
Fumaric	1—2	2	0.35	84	75
	2—3	1.81	0.37	95	100
Citraconic	1—2	2	0.59	50	55
	2—3	1.74	0.61	61	75
	7—8	03	0.37	80	75
Mesaconic	1—2	23	0.30	98	85
	2—3	1.86	0.31	108	100

at the electrode is effected in the same manner as in the pH-range 2.0 — 3.0. We have come to the conclusion from the mentioned results that the wave of investigated unsaturated acids in the pH-range 1.0 — 3.0 is the result of reduction of protonized acid molecules.

The second wave which appears at the pH of approximately 3 has a more negative half-wave potential, and it dominates at pH about 4, namely when in solution mostly monovalent acids ions are present. Hence we are of the opinion that the electrode process can be expressed by the scheme

$$AH^+ + H^+ \rightleftharpoons AH^{2+} \xrightarrow{2e} \text{product.}$$

Since in this pH-range there appear two, or even three waves, it would be too intricate to make calculations for proving that the second wave is the result of reduction of undissociated acid molecules. In addition to that, the second wave has at higher pH-values a kinetic character, which is probably a consequence of the slow rate of reaction of recombination of monovalent ions in molecules of acids.

At pH 3.5 to 3.9, depending on acid which is being reduced (except for mesaconic), the third wave appears. In the pH-range from 7.0 to 8.0 there are mostly bivalent acid ions present, so the electrode reaction can be expressed by the scheme:

$$A^{2-} + H^+ \rightleftharpoons AH^- \xrightarrow{2e} \text{product.}$$

The supposition that the third wave of maleic and citraconic acids or ginates from two-electron reduction of monovalent ions, is being confirmed by the data from Table II, proving that the theoretically calculated values from eq. (1) of the half-wave potential change in pH dependence are in proper agreement with the ex-

perimentally obtained results from the slope of the graphically presented dependences $E_{1/2} = f(pH)$.

The fact that the pH-values at which the first and second waves appear are infuenced by the buffer concentration, as in the case of 1 mol dm^{-3} buffer, can be explained bo the fact that the rate of ion recombination with protons is affected not only by the pH, but by the other Brönsted acids present.

ИЗВОД

ПОЛАРОГРАФСКО ПОНАШАЊЕ *ЦИС-* и *ТРАНС-*ДИКАРБОНСКИХ КИСЕЛИНА У ФОСФАТНОМ ПУФЕРУ

ИЛИНКА СПИРЕВСКА и ВЛАДИМИР Ј. РЕКАЛИЋ*

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Малеинска, фумарна, цитраконска и мезаконска киселина дају у фосфатном пуферу, завиено од pH-вредности и концентрације пуфера, један до три таласа. Испитивања су показала да су електродни процеси иреверсибилни, а да је гранична струја ограничена дифузијом, изузев у једној ужој области pH, где има кинетички карактер. На основу ових испитивања постављени су поступци за поларографско одређивање оба пара *цис-* и *транс-*изомера једног поред другог. Помоћу података о привидним поларографским дисоциационим константама, а сагласно закључцима Pospišil-a и Kuta-e и других учињен је покушај да се објасне електродни процеси.

(Примљено 1. јула 1983)

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