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# Polarographic Behavior and Determination of Vitamin $B_{13}$ in Aqueous Media at Dropping Mercury Electrode

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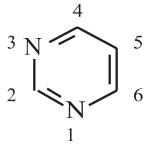
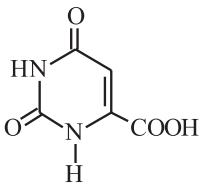
*Abstract.* The electrochemical reduction of Vitamin $B_{13}$ (orotic acid) at the dropping mercury electrode (DME) has been investigated. The polarographic behavior of orotic acid in Britton-Robinson (BR) buffer solutions (pH 2-12), in unbuffered solution, in acidic, and also in alkaline solution was measured. The study showed that, the effect of Hg-height on the limiting current and the effect of pH on each of the limiting current and the half-wave potential of the waves are diffusion controlled. The data also showed that under the optimum experimental conditions, a linear calibration graph was obtained on plotting the concentration of orotic acid versus the height of the reduction wave. A detailed mechanism for the reduction of orotic acid at the dropping mercury electrode correlating the nature of the orotic acid species and its reduction in different media, is proposed.

## Introduction

The electrochemical behavior of biologically important pyrimidine derivatives (pyrimidine ring structure I) that occurs in nature, have attracted much interest. For example, the uracin derivative orotic acid (2,4-dihydro-ox-pyrimidine-6-carboxylic acid, vitamin $B_{13}$ "structure II"), as an intermediate in the biosynthesis of unidine-5'-monophosphate (UMP), is the starting point for the biosynthesis of cytidine and thymidine nucleotides.




**structure I**



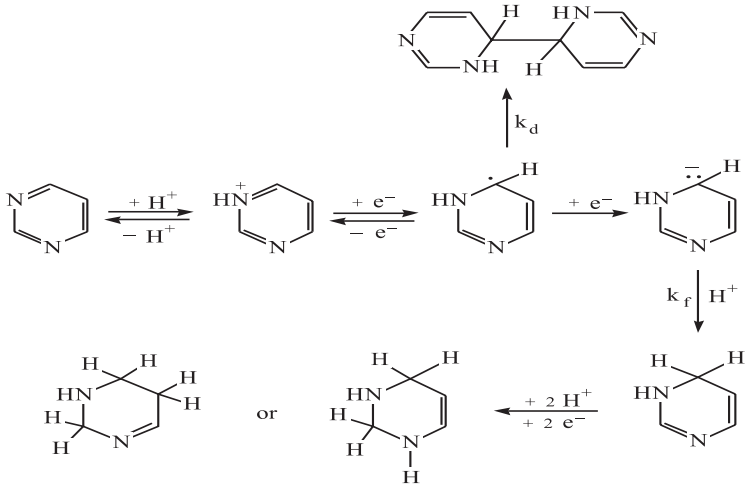

**structure II**

The polarographic reducibility of pyrimidine derivatives have been reported[1-2]. Elving *et al.*,[3-8] have studied the electrochemical reduction of purine and pyrimidine derivatives in nonaqueous and aqueous media. The reaction of purines in aqueous media is similar to that proposed for the electrochemical reduction of pyrimidine and other azabenzene[6] but in marked contrast to the behaviors of purines in media where free radical formation is not obtained due to prior protonation and initial multiple electron (2e or 4e) reduction. In another work[9] have studied the kinetics and mechanism of the electrochemical reduction of imidazole, pyrimidine and purine in aqueous media. The results indicated that imidazole did not show any faradic reduction in aqueous media within the available potential range. This lack of redox activity is to be associated with the aromatic nature of the five membered system which can exist in a large number of resonance forms. Pyrimidine on the other hand, is easily reduced to 1,4,5,6-tetrahydropyrimidine, and purine is catalytically hydrogenated apparently to the 1,6-dihydro derivative.

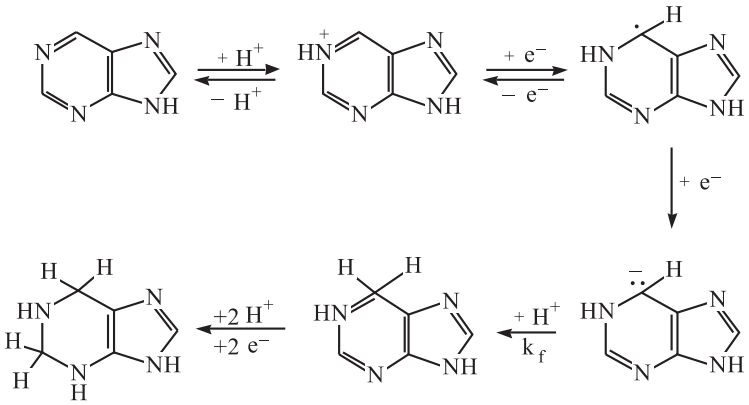
Imidazole itself shows little electroactivity, but the presence of the imidazole function as part of the purine molecule has a profound effect on the behavior of the latter. This is to be expected from the alteration in the electron densities in the pyrimidine ring when it is fused with the imidazole ring to form purine, *e.g.*, comparison of the calculated electron densities (π charges) for the ground state at the nine positions in purine and the corresponding positions in pyrimidine (π-deficient N-hetero-cycle) and imidazole (π-excessive N-hetero-cycle) indicate a flow of electrons from the imidazole region to the pyrimidine region of the purine[10]. As a result of the increased electron density the initial electrochemical reduction in aqueous media of purine was found more difficult than that of pyrimidine, even though the pyrimidine ring is involved in both processes. The potential required for the initial addition of an electron to purine is so much greater than in pyrimidine that the free radical species (or one derived from it by an exceedingly rapid chemical reaction) is immediately reduced, resulting in an initial two-electron reduction wave. The fact that the initial pyrimidine reduction (one-electron wave) is always easier, at more positive potential, than the initial purine reduction (two electron wave) may reflect the assisting action of the pyrimidine free-radical dimerization as well as electronic energy levels. The suggested mechanisms of the electrochemical reduction of pyrimidine and purine are given in Schemes 1 and 2, respectively.

The electrochemical reduction of substituted pyrimidines in acetonitrile with non-reducible groups have been reduced in a single, one electron, diffusion controlled process[11]. However, pyrimidine-4-carboxylic acid exhibited three reduction waves: a very down-out acid-reduction wave with unusual properties and, at more negative potential, an adsorption wave and a wave corresponding to the one-electron reduction of pyrimidine moiety.

Icha[12] has described the polarographic active behavior of orotic acid. Gupta *el al.*,[13] have also investigated the polarographic behavior of 5-nitroorotic acid in aqueous medium in the pH range[1-10]. The polarograms showed two well-defined steps up to pH 9.0, the first step is purely diffusion controlled (6-electron reduction) at all pH values, and the second step (4-electron reduction) is purely diffusion controlled in the acidic range with adsorption characteristics in the alkaline medium. Above pH 9.0, the compound was reduced in three steps : the first is purely diffusion controlled (4-electron reduction), the second (4-electron reduction) and the third (2-electron reduction) steps have adsorption character. Toshio and Soichiro[14] have studied the polarographic behavior and determination of orotic acid in milk by direct current polarography.




**Scheme 1. Electrochemical reduction of pyrimidine.**




**Scheme 2. Electrochemical reduction of purine.**

Calvo *et al.*,[1,15] have proposed a polarographic method for the determination of orotic acid in human serum and urine by differential pulse polarography. The electro-analytical behavior of orotic acid in the cathodic processes in HCl and in Britton-Robinson buffers at different pH's, using differential pulse polarography and cyclic voltametry techniques have been reported[16]. In another work[17] the same authors have studied the anodic wave of orotic acid by differential pulse polarography and cyclic voltametry.

The reduction potential in aqueous solution of orotic acid has been determined using the technique of pulse radiolysis with time-resolved spectrophotometric detection[18]. The electron adduct of orotic acid was found to undergo reversible electron exchange with a series of ring-substituted N-methylpyridinium cations with known reduction potentials. From the concentrations of orotic acid electron adduct and the reduced N-Methylpyridium compounds at electron-transfer equilibrium, the thermo-dynamical equilibrium constants were obtained and from these the reduction potentials.

This work is devoted to study the mechanism of the electro-chemical reduction of orotic acid at the dropping mercury electrode. The polarographic measurements will be recorded in different media to elucidate the nature of the orotic acid species and their reduction mechanism.

## Experimental

### *Materials*

Britton-Robinson buffers were prepared according to the standard procedure[19] with analar chemicals. Orotic acid (Sigma), all other reagents were of analytical-reagent grade. Bruker-type polarograph was used to record the polarograms.

#### *1 – The Dropping Mercury Electrode*

The rate of flow of mercury and the drop time were measured at mercury height of 30 cm. The rate of flow of mercury was measured as reported[22]. Drop time was measured at a potential corresponding to a point in the upper plateau of the wave. No single value can be reported because the increase of the pH of the solution leads to the shift of the wave to more negative potential, and these result in variation of the drop time. Extreme values of t = 4.5 sec at –1.0 V and t = 3.6 at –1.5 V (vs. SCE).

#### *2 – Electrolysis Cell*

A standard three electrode electrochemical cell was used, the working electrode was dropping mercury, the auxiliary electrode is a platinum, and the reference electrode is an aqueous saturated Calomel.

*3 – Preparation of Solutions*

A $2 \times 10^{-3}$ M stock solution of the orotic acid (Sigma) was prepared by dissolving an appropriate amount of orotic acid in distilled, deionized water. Universal (Britton-Robinson) buffers were prepared according to the standard procedure (19) with analar chemicals. All the other reagents were of analytical-reagent grade.

*4 – Recording of Polarograms*

Dissolved oxygen was removed by passing through the test solution a stream of purified argon for 25 min. The solution was protected from the atmosphere during the electrolysis by passing a steady stream of purified argon over the surface. The polarograms were obtained using Bruker-type polarograph at (25 ± 02)ºC.

## Results and Discussion

### *I – Polarographic Behavior of Vitamin $B_{13}$ (Orotic Acid) in (Britton-Robinson) Buffer*

The polarograms of orotic acid in (Britton-Robinson) buffer covering the pH 2-12 are shown in Fig. 1. The compound showed well defined wave at pH less than 4.0. However, in the pH range 4.0-4.8, a second wave appears at more negative potentials and the increase of the pH of the solution leads to a decrease in the height of the first wave and increase of the height of the second one. The polarograms showed also that at pH 4.8 a third wave appears at more negative potentials and orotic acid is reduced through three well-defined polarographic waves. A further increase of the pH of the solution from 4.8 to 7.0 leads to the disappearance of the first wave and the polarograms showed only two waves. Above pH 7.0 the second wave also disappeared and the polarographic reduction of orotic acid in Britton-Robinson buffer takes place through a well-defined wave at more negative potentials.

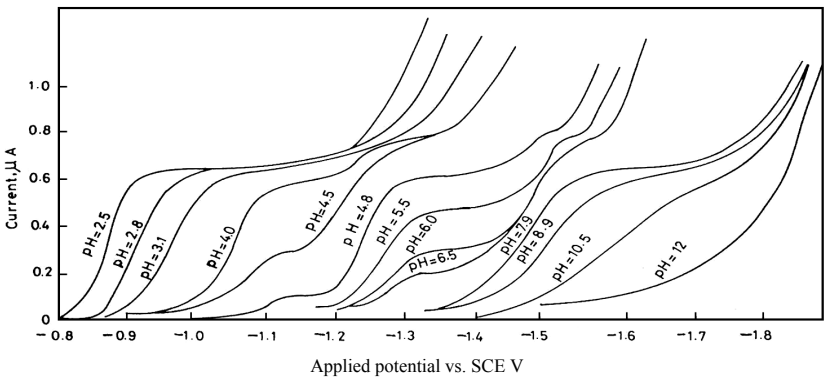



**Fig. 1. Polarogram $1 \times 10^{-4}$ orotic acid in Britton-Robinson buffers at different pH's.**

To investigate the nature of the orotic acid species and the mechanism of reduction of these species at the dropping mercury electrode in Britton-Robinson buffer solutions in the pH range 2-12, (i) the effect of Hg-height on the limiting current, (ii) the effect of pH on the limiting current, (iii) analysis using the fundamental wave equation, and finally (iv) the effect of pH on the half-wave potentials of the three waves will be discussed below.

*(i) Effect of Hg-Height on the Limiting Currents of the Three Waves*

The effect of the height of the mercury column above the capillary tip can be used to investigate the nature of the polarographic wave. The value of the parameter x in the equation, $i = k\, h^x$ [20-23] (where h is the height of the mercury column and k is a constant) indicates the nature of the wave. When x = 0, the reduction process is controlled by a kinetic reaction; if x = 0.5, the reduction process is controlled by the diffusion of the electro-active species from the bulk solution to the electrode surface; and when x = 1.0, the process is controlled by the adsorption of the reducible species at the mercury/solution interface.

Figure 2 showed the plot of log $i_l$ versus log h for the first wave of orotic acid in Britton-Robinson buffer of pH = 2.30, pH = 4.3, and pH = 8.9 respectively. As shown in Fig. 2 the plot was found linear and the slope x = 0.68, indicating that the reduction of orotic acid at the dropping mercury electrode is mainly controlled by the diffusion of the orotic acid species from the bulk solution to the electrode surface. Similar behavior was observed at pH 4.3 and 8.9 for the second and third waves of orotic acid respectively. As the plots are linear and the slope x = 0.61 for the second wave however, x = 0.65 for the third wave indicating that the reduction processes corresponding to these two waves are controlled also by the diffusion of the orotic acid species from the bulk solution to the electrode surface.

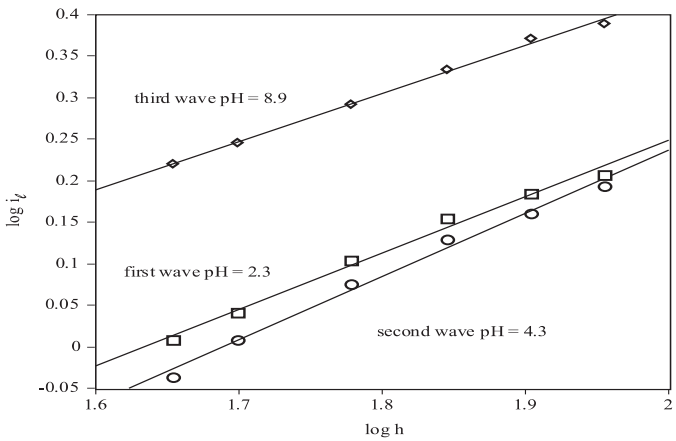
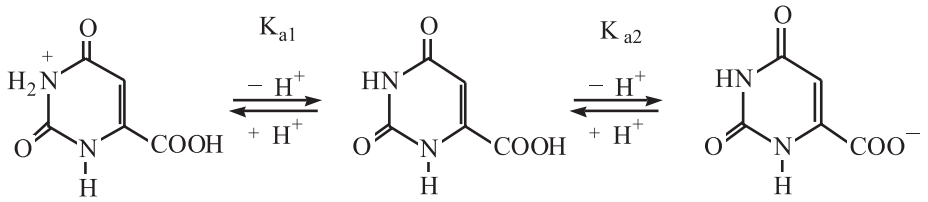



**Fig. 2. Effect of the Hg-height on the logarithm of the limiting current ($i_l$) of the first wave, second wave, and third wave of orotic acid in Britton-Robinson buffer at the pH's shown.**

*(ii) Effect of pH on the Height of the Three Waves*

Figure 3 and Table 1 give the effect of pH on the heights of the three polarographic reduction waves of orotic acid. The figure showed that in the pH range 3-4.5 the height of the second wave increases on the expense of height of the first one. However, in the pH range 4.5-5.0, the height of the second wave is nearly constant but the height of the third wave increases on the expense of the height of the first one increasing the pH of the solution. At pH's higher than 5.0, the first wave disappeared and the height of the third wave increased on the expense of the height of the second one increasing the pH. The figure shows also that the total limiting current of all the waves at different pH's is nearly constant and equal about 0.7 μA. Therefore, different reducible species of orotic acid are present in equilibrium, and the percentage of each one depends on the solution pH[21]. These species are probably the protonated, the neutral and the deprotonated orotic acid. The equilibria between these complex species can be represented in Scheme 3 as follows :




**Scheme 3. Chemical equilibria between the protonated, neutral and deprotonated species of orotic acid in solution.**

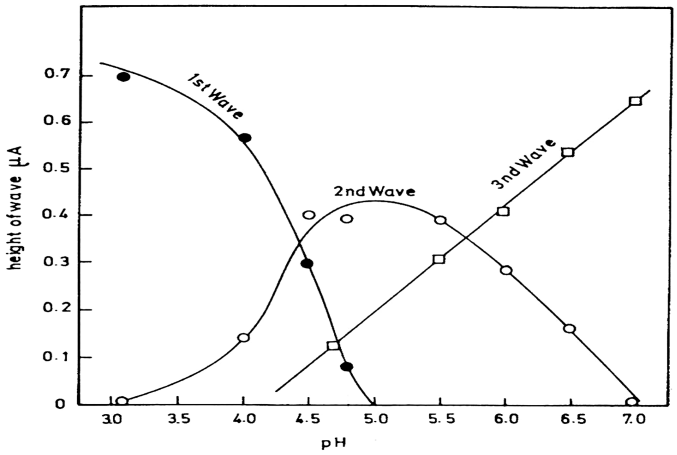



**Fig. 3. Effect of pH on the Hg-height of the three waves of $1 \times 10^{-4}$ M orotic acid in Britton-Robinson buffer.**

**Table 1. Effect of pH on the height of the peak current of the three waves of orotic acid in Britton-Robinson Buffer.**

| pH | id, µA | | |
|---|---|---|---|
| | First wave | Second wave | Third wave |
| 3.1 | 0.70 | – | – |
| 4.0 | 0.56 | 0.14 | – |
| 4.5 | 0.30 | 0.40 | – |
| 4.8 | 0.08 | 0.39 | 0.13 |
| 5.5 | – | 0.39 | 0.31 |
| 6.0 | – | 0.28 | 0.42 |
| 6.5 | – | 0.16 | 0.54 |
| 7.0 | – | – | 0.70 |

The first equilibrium appears in the pH range 3-5 with the $pK_{a1}$ equals about 4.4, while the second equilibrium appears in the pH range 5.0 - 7.0 with $pK_{a2}$ equals about 5.7.

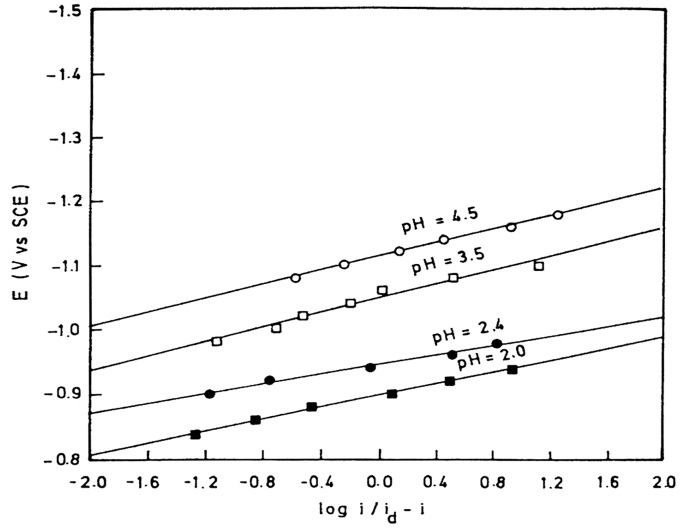
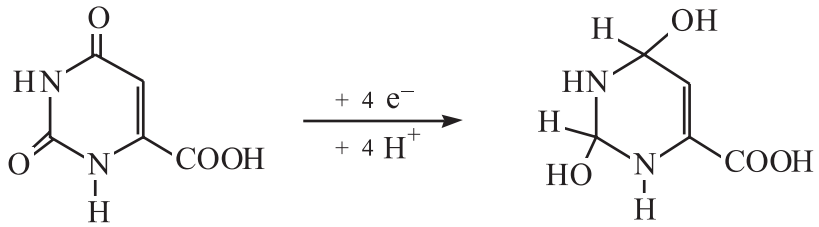



**Fig. 4. Analysis of first wave of orotic acid in Britton-Robinson buffer at different pH's.**

The constancy of the total limiting current of the three waves at different pH's indicated that the three species of orotic acid (Scheme 3) are probably reduced by the same mechanism and consuming the same number of electrons. On the basis of mechanism suggested[8], for the reduction of pyrimidine derivatives in the aqueous solution, the reduction of the orotic acid molecule most probably consumes four electrons and can be represented in Scheme 4 as follows :




**Scheme 4. Proposed mechanism for the reduction of orotic acid.**

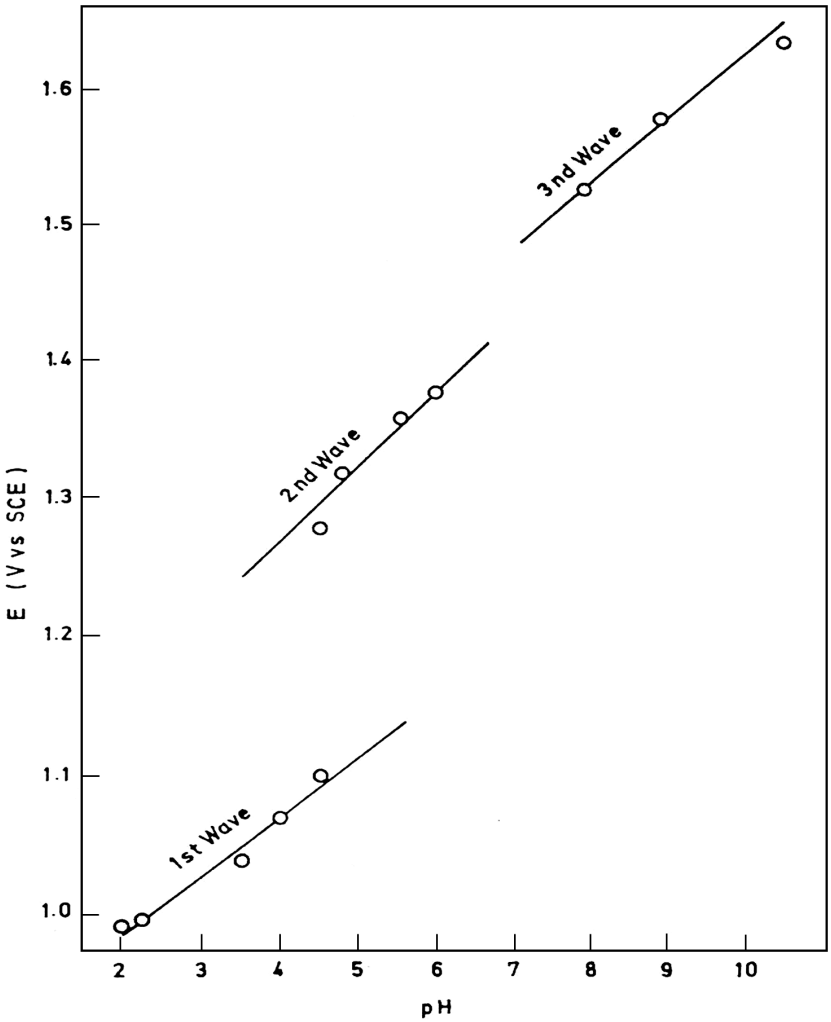



**Fig. 5. Effect of pH on the Hg-height of the half-wave potentials of the three waves of orotic acid in Britton-Robinson buffer.**

To investigate the detailed mechanism of the reduction of orotic acid, the analysis of the waves at different pH's and the effect of pH on the half-wave potentials of the three waves are critically studied and discussed below.

*(iii) Analysis of the Waves*

The fundamental wave equations for the reversible and irreversible reduction processes at 25ºC are given in the form[23, 24].

$$E = E_{1/2} - \frac{0.059}{n} \log \frac{i}{i_d - i}$$

$$E = E_{1/2} - \frac{0.059}{\alpha\ n_a} \log \frac{i}{i_d - i}$$

where E is the potential, $E_{1/2}$ is the half-wave potential of the wave, i is the current corresponds to a certain potential in the rising part of the wave, $i_d$ is the diffusion current, and n is the number of electrons consumed in the reduction of the reduced particle, $\alpha$ is the transfer process and $\alpha\ n_a$ is the number of electrons consumed in the rate-determining step of the reduction reaction.

Plots of E versus log $[i/(i_d - i)]$ for the three reduction waves of orotic acid at different pH's, were linear. Representative plots are given for the first wave in Fig. 4. The values of the slopes are given in Table 2 for the three waves. The values of the slopes were found in the range of 0.045-0.056 for the first wave, 0.045-0.0600 for the second wave and 0.052-0.085 for the third wave (Fig. 5). Therefore, the values of the slope of the plots of E versus log $[i/(i_d - i)]$ indicates that the three waves are irreversible in nature. The number of electrons consumed in the reduction of orotic acid is proposed to be four in accordance with previous discussion.

**Table 2. The slope of the plot E versus log $[i/(i_d - i)]$ and $\alpha\ n_a$ parameter for the three waves of orotic acid and in Britton-Robinson buffer at different pH's.**

| pH | First wave | | Second wave | | Third wave | |
|---|---|---|---|---|---|---|
| | Slope | α na | Slope | α na | Slope | α na |
| 2.0 | 0.045 | 1.3 | – | – | – | – |
| 2.4 | 0.045 | 1.3 | – | – | – | – |
| 3.5 | 0.056 | 1.06 | – | – | – | – |
| 4.5 | 0.054 | 1.09 | 0.045 | 1.3 | – | – |
| 4.8 | – | – | 0.046 | 1.28 | 0.052 | 1.13 |
| 5.5 | – | – | 0.053 | 1.11 | 0.067 | 0.88 |
| 6.0 | – | – | 0.061 | 0.96 | 0.077 | 0.77 |
| 6.5 | – | – | 0.045 | 1.30 | 0.071 | 0.83 |
| 7.9 | – | – | – | – | 0.060 | 0.98 |
| 8.9 | – | – | – | – | 0.068 | 0.86 |
| 10.5 | – | – | – | – | 0.085 | 0.69 |

The values of the $\alpha\, n_a$ parameter for the three reduction waves of orotic acid at different pH's were found in the range of 1.06 - 1.30 for the first wave; 0.96 - 1.30 for the second wave; and for the third wave, it is in the range of 0.69 - 1.13. The values of $\alpha\, n_a$ parameter of the three waves indicate that the rate determining step of the reduction process of the orotic acid species most likely consumes two electrons, because the value of the transfer coefficient a is always near 0.5[24].

*(iv) Effect of pH on the Half-Wave Potentials of the Waves*

To suggest the proper mechanism of the reduction of orotic acid, the number of protons consumed in the rate determining step were calculated from the data of the effect of pH on the half-wave potentials of the three waves, Figure 9 showed the relations between the half-wave potentials of the three waves of orotic acid and the pH of the BR buffer. A linear dependence of the $E_{1/2}$'s of the three waves on the pH of the solution was observed. The slope of the lines $[\Delta E_{1/2}/\Delta pH]$ for the three waves were found equal 0.045, 0.054, and 0.050 for the first, the second and the third wave, respectively.

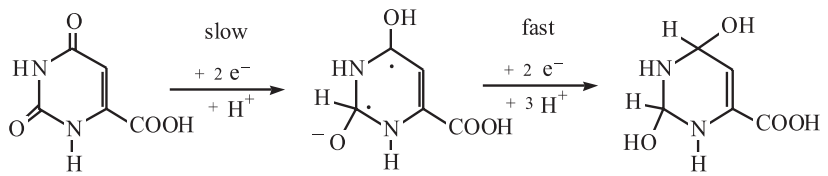
To calculate the number of protons consumed in the rate-determining step of an irreversible reduction process the following relation is applied at 25ºC[22, 23].

$$\frac{\Delta E_{1/2}}{\Delta pH} = \frac{0.059}{\alpha\ n_a}\ p$$

where p is the number of protons consumed in the rate-determining step of the reduction process.

Using the values of $[\Delta E_{1/2}/\Delta pH]$ and $\alpha\, n_a$ parameter (Table 2) for each wave in the above a value of p in the range of 0.8 - 1.0 for the first wave, and 0.9 - 1.2, and 0.6 - 1.0 for the second and third wave, respectively. Thus, the rate-determining step of the reduction of the orotic acid species at the dropping mercury electrode probably consumes one proton.

The most probable mechanism for the reduction of orotic acid molecule at the DME can be suggested on the basis that, the rate-determining step consumes one proton and two electrons and the total number of electrons consumed in the over all reduction process is four and the effect of pH on the height of the three waves is given as follows :



## *II – Polarographic Behavior of Vitamin $B_{13}$ (Orotic Acid) in Acidic and Alkaline Solutions*

Figure 6 shows the polarogram of $1 \times 10^{-4}$ M orotic acid in 0.1 M NaOH. The polarogram contains only the hydrogen evolution curve, indicating that in the alkaline solutions, the orotic acid species is electrochemically inactive in the available range of applied potential (about –2.0 V vs SCE).

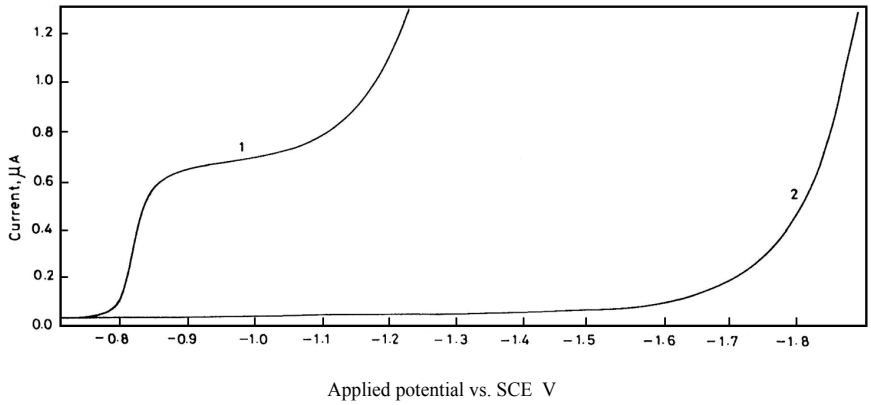



**Fig. 6. Polarograms of $1 \times 10^{-4}$ M orotic acid in 0.1 M HCl (1) solution and in 0.1 M NaCl (2).**

On the other hand, the polarographic reduction of orotic acid $1 \times 10^{-4}$ M in 0.1 M HCl takes place through one defined wave at about –0.8 V (*vs.* SCE). The limiting current of this wave is near 0.7 µA. The linear dependence of Hg-height with the limiting current (Fig. 7) where x = 0.61 indicated that the reduction process corresponding to this wave is mainly diffusion controlled.

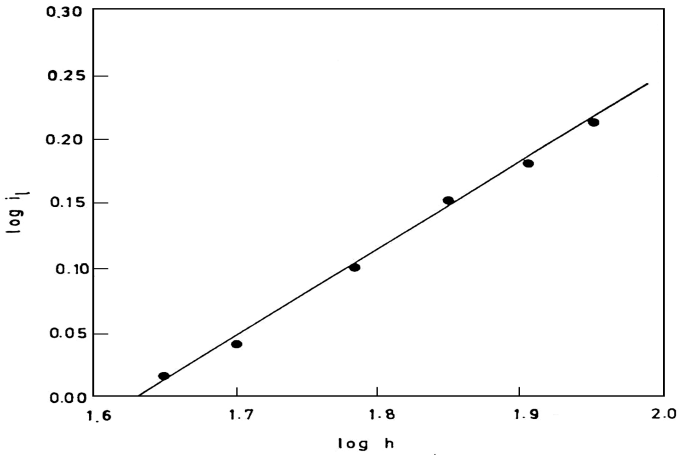



**Fig. 7. Effect of the Hg-height on the logarithm of the limiting current ($i_\ell$) of the second wave of orotic acid in 0.1 M HCl solution.**

The polarographic behavior of orotic acid in 0.1 M HCl is quite similar to its behavior in BR buffer solutions of pH less than 3.0. Orotic acid in the acidic medium is probably present in the protonated form which is reduced at the DME through four-electron wave and the reduction process most probably proceeds as follows :

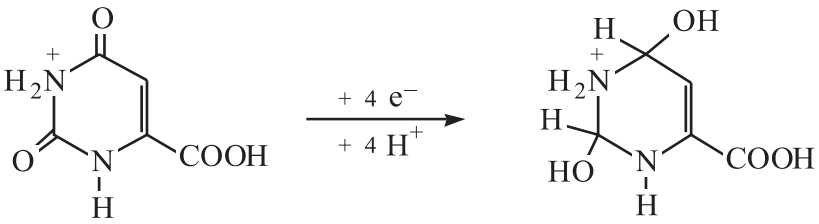



Figure 8 showed the effect of the concentration of orotic acid on the height of its polarographic reduction wave. The height of the wave is directly proportional to the concentration of orotic acid. The dependence of the diffusion current of the reduction wave of orotic acid on its concentration is given in Fig. 9. The plot of the diffusion current versus the molarity of solution was linear. The regression analysis of the plot revealed that the intercept equals zero and the slope is equal $4.74 \pm 0.02 \times 10^3$ μA $mol^{-1}$ $l^{-1}$. This indicates that the concentration of orotic acid can be determined polarographically.

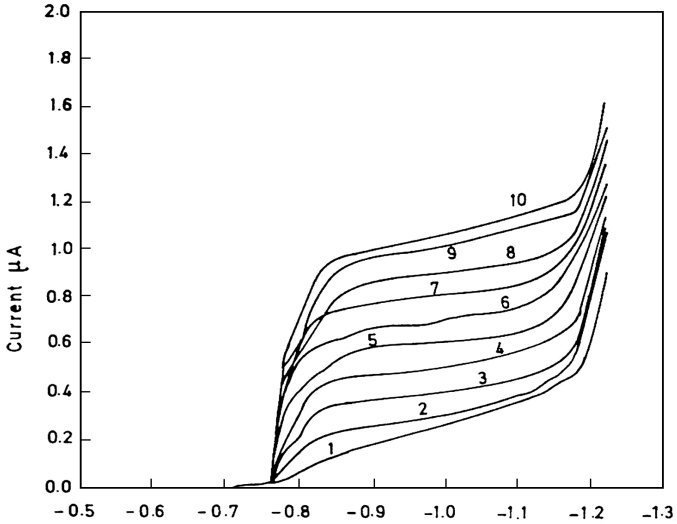



**Fig. 8. Polarograms of various concentrations of orotic acid in 0.1 M HCl:**
**1) $2 \times 10^{-5}$ M, 2) $4 \times 10^{-4}$ M, 3) $6 \times 10^{-5}$ M,**
**4) $8 \times 10^{-5}$ M, 5) $2 \times 10^{-4}$ M, 6) $1.2 \times 10^{-4}$ M,**
**7) $1.4 \times 10^{-4}$ M, 8) $1.6 \times 10^{-4}$ M, 9) $1.8 \times 10^{-4}$ M,**

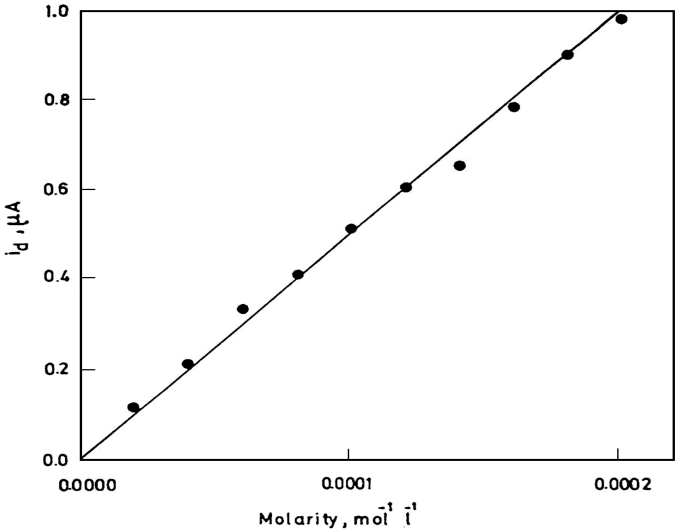
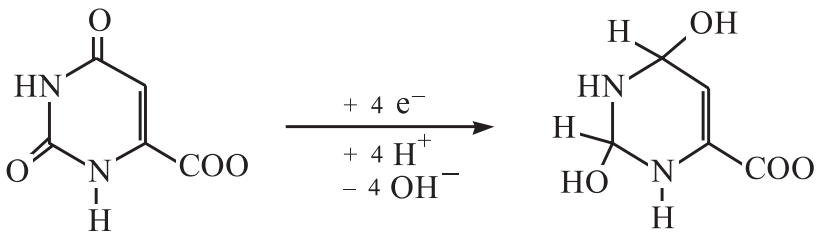



**Fig. 9. Effect of the concentration of orotic acid on the diffusion current of the polarographic wave in 0.1 M HCl solution.**

### *III – Polarographic Behavior of Orotic Acid in Neutral Unbuffered Solution*

Figure 10 shows the polarogram of $1 \times 10^{-4}$ M orotic acid in 0.1 M KCl solution. This well defined wave at about –1.4 V (vs. SCE) was observed. The effect of Hg-height on the limiting current of this wave (Fig. 11) gives x = 0.66, indicating that the reduction process corresponds to this wave is mainly diffusion controlled. The value of the limiting current of the wave is about 0.7 μA and equal to the limiting current of the polarographic reduction wave of orotic acid in BR buffer at pH ≥ 7.0. This behavior indicates that the total number of electrons consumed in the reduction of orotic acid in 0.1 M KCl is four electrons and the acid is present in the form of caboxylate anion. The reduction process can be represented as follows :



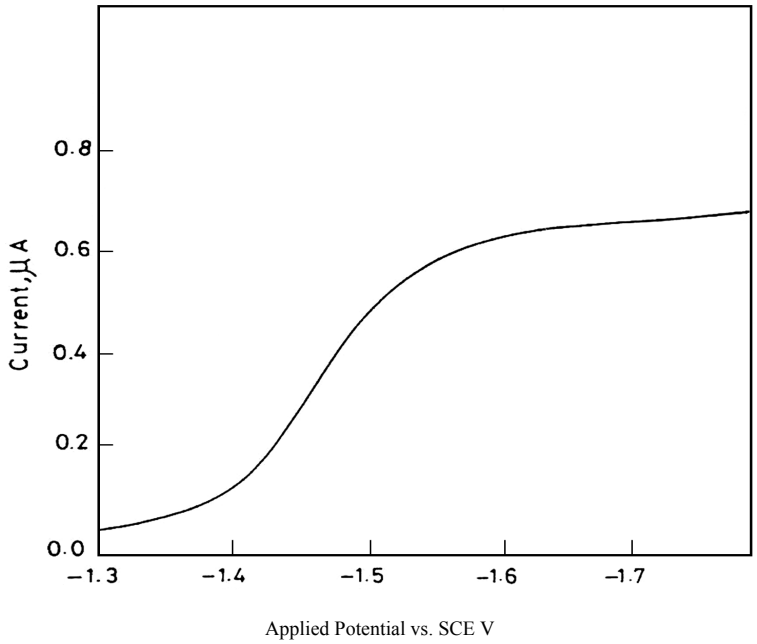



**Fig. 10. Polarogram of $1 \times 10^{-4}$ M orotic acid in 0.1 M KCl.**

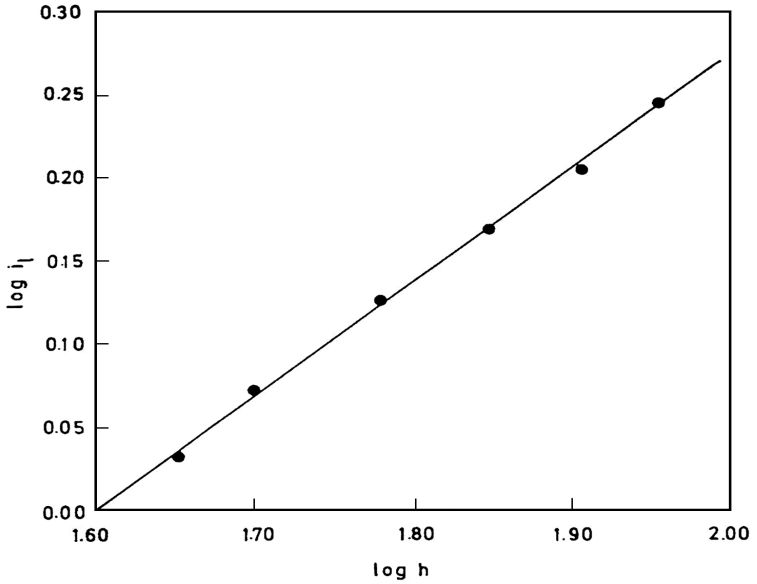



**Fig. 11. Effect of the Hg-height on the limiting current of the wave of orotic acid in 0.1 M KCl solution.**

## Conclusion

The polarographic behavior of vitamin $B_{13}$ has been investigated at the DME in BR buffers having pH 2-12, HCl (0.1 M), NaOH (0.1 M) and in neutral unbuffered KCl (0.1 M) solutions.

A mechanism of the reduction of orotic acid at the DME has been proposed on the basis that the slow step consumes two electrons and one proton and the overall reduction reaction consumes four electrons and four protons.

Orotic acid in 0.1 M HCl is present in the protonated form and is reduced at the dropping mercury electrode through four electron wave. The plot of the orotic acid concentration versus the diffusion current in 0.1 M HCl was linear. The regression analysis revealed that, the intercept is equal to zero and the concentration of orotic acid can be determined polarographically.

The polarographic behavior of orotic acid in 0.1 M KCl solution is quite similar to its behavior in Britton-Robinson buffer at pH $\geq$ 7.0. Orotic acid in neutral unbuffered solutions is present in the carboxylate anion and reduced at the dropping mercury cathode through four electron wave.

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# السلوك البولاروجرافي وتعيين فيتامين ب-١٣ في وسط مائي عند قطب الزئبق المتساقط

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*المستخلص.* تضمن البحث دراسة الاختزال الكهروكيميائي لفيتامين ب-١٣ (حمض الأوروتيك) عند قطب الزئبق المتساقط، ومن ثم قياس السلوك البولاروجرافي لحمض الأوروتيك في محاليل بريتون وروبنسون المنظمة (Britton-Robinson Buffers) ذات الأرقام الهدروجينية (٢-١٢)، وفي محول غير منظم، وفي محلول حمضي قوي وقلوي. أظهرت الدراسة تأثير ارتفاع عمود الزئبق على التيار النهائي في عملية الاختزال، وتأثير الرقم الهيدروجيني على كل من التيار النهائي وجهد منصف الموجة للموجات البولاروجرافية، وأن الاختزال تحكمه عملية الانتشار (diffusion controlled). أظهرت الدراسة أيضًا وجود علاقة خطية بين تركيز حمض الأوروتيك على التيار والتيار النهائي للموجات البولاروجرافية. تم اقتراح آلية (mechanism) مفصلة لاختزال حمض الأوروتيك عند قطب الزئبق المتساقط بناءً على طبيعة حمض الأوروتيك، ومدى اختزاله في الأوساط المختلفة.