

Electrochemical behavior of some new pyrimidine derivatives

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Abstract: Electrochemical reduction of two recently synthesized pyrimidine compounds, 1-amino-5-benzoyl-4-phenyl-1H-pyrimidine-2-one (**I**), and 1-amino-5-benzoyl-4-phenyl-1H-pyrimidine-2-thione (**II**) were investigated by cyclic voltammetry at a hanging mercury drop electrode in aqueous methanol (36 % v/v) and in non-aqueous methanol. A series of cathodic peaks without the corresponding anodic peaks were observed for **I**. As the pH of the solution was increased, some of the cathodic peaks overlapped resulting in the loss of the previously observed peaks. For **II**, three cathodic peaks and one anodic peak were observed in addition to those observed for **I**. The peak potentials shifted in the negative direction with increasing pH. This shift was measured over a large pH range (1.80 – 12.30) to determine the pK_a values of the compounds. The acidity constants related to the amino groups were 4.80 and 9.80 for **I** and 5.50 and 9.80 for **II**. A thiol-thione tautomerization was observed for **II**, which was more pronounced in the non-aqueous methanol medium. The pK values for both protonation and deprotonation of the thiocarbonyl group were also determined. The pK values were 5.80 and 9.80 for protonation and deprotonation in aqueous methanol and 6.80 and 10.80 in non-aqueous methanol.

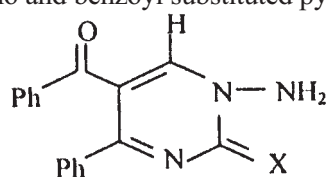
Keywords: pyrimidine-one, pyrimidine-thione, pyrimidine bases, cyclic voltammetry, hanging mercury drop electrode.

INTRODUCTION

Since pyrimidine bases are minor constituents of nucleic acids, the chemistry of pyrimidines has been the subject of much research owing to their applications in molecular biology, and medicine.¹ They show many activities, including antibacterial, antifungal, antiviral, insecticidal and mitocidal effects,^{2,3} and colony inhibition.⁴ Moreover, some divalent transition metal complexes (Cu^{2+} , Zn^{2+} , Cd^{2+} , Co^{2+} , Hg^{2+} , UO_2^{2+} , etc.) of pyrimidine play an important role in the maintaining of functionalities of DNA, as well as being used in the preparation of pesticides.^{5–10} These findings stimulated our interest in this study to isolate and characterize the electrochemical behavior 1-amino-5-benzoyl-4-phenyl-1H-pyrimidine-2-one (**I**), and 1-amino-5-ben-

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zoyl-4-phenyl-1H-pyrimidine-2-thione (**II**). The structures of the investigated compounds are given in Scheme 1. Studies of the electrochemistry of pyrimidine derivatives, especially thiopyrimidines and derivatives in aqueous solutions^{5,11-19} and nonaqueous solutions,²⁰⁻²³ are limited. Moreover, most of these studies were carried out over a narrow potential range and none of these studies investigated the electrochemical properties of amino and benzoyl substituted pyrimidine derivatives.



X=O (**I**)

X=S (**II**)

Scheme 1.

Of all organic solvents, methanol is the closest to water in structure and properties,²⁴ therefore, the investigations were performed mainly in a mixture of methanol–water (36 % v/v methanol). Non-aqueous methanol medium was also used to understand the effect of the solvent media on the peak characteristics and acidity constants. The effect of pH on the voltammetric characteristics of the compounds was investigated by varying the pH of the medium from pH 1.80 to 12.80. In addition to cyclic voltammetry, controlled potential electrolysis was performed and the electrochemical reduction products were examined by UV and IR for a comprehensive understanding of the peak characteristics.

EXPERIMENTAL

Materials and solutions

The synthesis of the compounds have been described elsewhere.^{2,3} Their purity was tested by thin-layer chromatography using the solvent mixtures methanol – chloroform (1:9 v/v) and methanol – benzene (1:9 v/v) and verified by IR data.

The compounds were insoluble in water, therefore, stock solutions were prepared in an appropriate volume of methanol from which working solutions were prepared daily in the concentration range between C1: 3.556×10^{-5} and C3: 7.112×10^{-5} M for compound **I** and between C1: 4.568×10^{-5} and C3: 9.760×10^{-5} M for compound **II**, to give a final alcohol content of 36 % by volume. Triply distilled water was used for the measurements in aqueous medium. Mercury was purified electrochemically using the procedure described by M. E. Hanke.²⁵ The ionic strength was kept constant at 0.1 M in the experiments using LiCl as supporting electrolyte. All measurements were carried out at room temperature.

All chemicals were obtained from Fluka, as reagent grade materials. Methanol was used after distilling. Argon was purified and equilibrated by bubbling it successively through alkaline pyrogallol solution, sulfuric acid, distilled water and finally a portion of the working solution. During the measurements, the solutions were protected under an argon atmosphere.

Apparatus

Cyclic voltammetric and coulometric measurements were carried out using a DT 2101 Model Potentiostat and a PPR1 Model Wave Generator. A three electrode cell system consisting of a satu-

rated calomel electrode (unless otherwise stated) as the reference electrode and a coil of platinum wire as the counter electrode was used. The working electrode was a stationary hanging mercury drop electrode (hmde) with a surface area of 0.0445 cm². The pH(R)²⁶ of the solutions were measured using a digital pH meter (Hanna Instruments 8314, Italy; ± 0.01 pH unit) and a combined pH electrode that was standardized using standard aqueous buffers (pH 4.00, 9.00).

Cyclic voltammograms were recorded on a YEW 3022 Model (Yogokawa Hokushin Electric) A4 x-y recorder and the controlled potential electrolysis recordings were recorded on a YEW 3021 Model (Yogokawa Hokushin Electric) y-t recorder.

A Shimadzu double beam 1601 UV-VIS spectrophotometer with quartz cells (1-cm path length) was used for the UV/VIS spectroscopic measurements. A Mattson 1000 FTIR spectrometer was used for the IR measurements.

Buffer solution

Working solutions were buffered with Britton-Robinson,²⁶ (B.R.), buffer solution composed of a mixture of glacial acetic acid, orthophosphoric acid and boric acid (0.04M in each, in the final solution) in the pH range of 1.80–12.30. For the experiments performed in non-aqueous methanol, the B.R. buffer did not contain orthophosphoric acid due to the precipitation which occurred upon addition of solid sodium hydroxide.

The ionic strength of the working solutions was kept constant at 0.1 M with LiCl and the pH was adjusted with solid sodium hydroxide. To prepare the working solution, the pH(R) of the working solution was first adjusted to the desired pH(R) by dotting with a relatively concentrated KOH on a thin glass rod, and then 27 ml of this solution was transferred to the compartment.

Measurements

For each compound, cyclic voltammograms were recorded for different concentrations and at different scan-rates in the pH range between 1.80 and 12.30. Voltammetric scans were done at five different scan rates in the range of 40 – 400 mV/s. A cathodic scan was made first by varying the potential from 0 to –2000 mV, and then reversed to the anodic direction.

Electrode preparation

A working electrode was prepared for each run. To form a sessile drop, a micrometer-type syringe was used.²⁷ For each run, a new mercury drop was hung up to the surface of the mercury-film coated electrode to achieve reproducibility. The hang up operation was done just before each run by dropping mercury into a petri dish containing triply distilled water. The remaining mercury in the dish was discarded.

Procedure

An appropriate (27 ml) volume of working solution was placed into the cell. Air was removed by purging argon through the cell for 10 min for aqueous–methanol solutions and 20 min for the non-aqueous methanol. A freshly prepared working electrode (hmde) was inserted rapidly into the appropriate compartment of the cell and the argon flow was stopped. The cathodic scan was performed after 5 s rest-time to record the corresponding cyclic voltammograms. A blank solution was studied identically to obtain a background curve. The peak potentials, E_p , and peak currents, I_p were determined after subtraction of the background current.

Controlled-potential electrolysis experiments

The quiescent cathode area of the mercury pool was 12 cm². The electrolysis experiments were carried only in the aqueous methanol medium. The pH of the solution was 3.50 for peak Ia and 3.80 for peak IIa. The electrolysis potentials were –0.742 and –0.690 V (vs. Ag|AgCl|KCl_{SAT}) corresponding to the crests of Ia and IIa, respectively. Controlled-potential electrolysis was not successful for the other peaks. By using the procedure outlined by Lingane,²⁸ the number of electrons involved in the reduction was found to be 1.418 and 2.02 for Ia and IIa, respectively.

The course of the electrolysis was followed by recording the voltammetric curves and the UV spectra before and after the electrolysis. Identification of the stable products was performed by thin-layer chromatography and IR spectroscopy. The completeness of the electrolysis experiments was monitored voltammetrically by the disappearance of the peak from the voltammogram.

RESULTS AND DISCUSSION

Preliminary experiments showed that the peak currents (I_p) of each compound increase steadily with increasing compound concentration. The rate of increase in I_p was very small for concentrations above 7.112×10^{-5} M for **I**, and 5.488×10^{-5} M for **II**. Thus, the concentrations of the compounds were kept as low as possible to obtain reproducible results and very clean mercury was used. A voltammogram for each compound obtained at different pH values is given in Fig. 1.

Initial studies were carried out in a medium that did not contain any supporting electrolyte, LiCl and B.R. buffer, as well as in a medium containing only LiCl to examine if any of the peaks observed originated from a possible reaction between

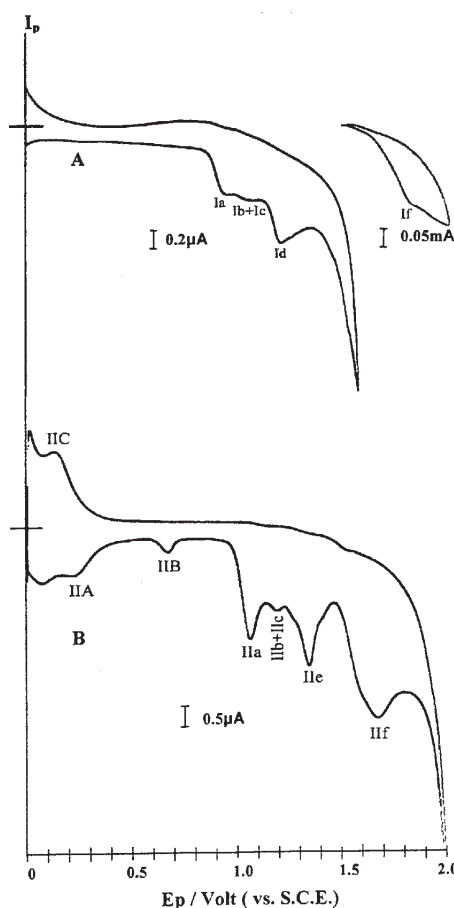


Fig. 1. Cyclic voltammograms; A for **I**: ($v = 0.080$ V/s, pH 5.80, $c = 7.112 \times 10^{-5}$ M). B for **II**: ($v = 0.080$ V/s, pH 7.50, $c = 5.488 \times 10^{-5}$ M).

the compound and the supporting chemicals. It was found that there were no reactions between the compounds and the supporting electrolytes.

In aqueous methanol, various cathodic peaks (Ia – If) of different magnitude were observed for compound **I**, in the potential range studied. No anodic peak was observed for this compound. Ic was the smallest peak that merged with Ib at a pH around 4.80 and the merged peak disappeared as the pH increased above 8.80. Peaks, Ia, Id and If, were observed at all pH values studied. Of all the peaks observed for compound **I**, peak If showed the highest current. The same peak, on the other hand, was observed as a very small peak in the non-aqueous methanol medium.

In the aqueous methanol medium, the peaks, Ila, Ilb, Ilc and IIf observed for compound **II** were identical with those (*i.e.*, Ia, Ib, Ic and Ig) observed for compound **I**. No peak was observed for **II** that is identical to Id of compound **I**. On the other hand, compound **II** showed two cathodic peaks (IIA, IIB) and an anodic peak (IIC) at highly positive potentials. Additionally, a small cathodic peak (IIe) was observed of **II** at a much more negative potential than that of Ilc, Ilc also exhibited smaller currents than the other peaks. It merged with Iib and at a pH of around 4.80 and the merged peak disappeared completely at pH values above 7.80. Ic and Iic were not observed in non-aqueous methanol. Ila and IIf peaks were very sharp and well-defined at all investigated pH values. Of all the peaks observed with **II**, peak IIf had the highest current values.

The voltammetric results showed that electron transfer processes were mainly accompanied by protonation. It was also found from the voltammograms that the processes generally displayed an irreversible behavior which indicated the occurrence of adsorption in the reaction mechanism. The information obtained for identical peaks of compound **I** and **II** are compared below.

Peaks Ia and Ila: In aqueous methanol, peak Ia was observed as a broad peak up to pH 4.30, and became sharper as the pH increased. The peak shape was well defined in both aqueous methanol and non-aqueous methanol medium. Peak Ila, on the other hand, was sharp and well defined in aqueous methanol up to pH 7.50 after which the peak broadened with increasing pH. In non-aqueous methanol, Ila was well defined up to pH 4.80. As the pH increased, the peak became L-shaped and then disappeared above pH 6.80.

Figures 2 and 3 show I_p vs. pH and E_p vs. pH plots for Ia and Ila, respectively. The respective equations for $E_p = f(\text{pH})$ variations are summarized in Table I. The transfer coefficients, αn_a values were computed using²⁷ $E_p - \ln v$. The αn_a values for **I** were 1.35 at pH 3.80 and 1.15 at pH 11.80. For compound **II**, they were 0.77 at pH 2.50 and 0.89 at pH 11.50. The number of protons transferred, P , was found to be about 1 (≈ 1.37 for Ia and 0.8 for Ila) for both peaks when the above given αn_a values and the slopes given in Table I were substituted into the following equation.²⁹

$$dE_p/d(\text{pH}) = (-0.059/\alpha n_a)p \quad (1)$$

For both Ia and IIa, the I_p values were found to be pH dependent within the examined pH range. As shown in Fig. 2, the I_p for Ia increased from pH 3.30 to 10.30. Above pH 10.30, the magnitude of I_p decreased due to the decrease in the protonation reaction rate as the solution became more alkaline. For IIa (Fig. 3), however, I_p decreased from pH 3.80 to 9.80. This discrepancy was attributed to the presence of the carbonyl group at position 2- of compound I.

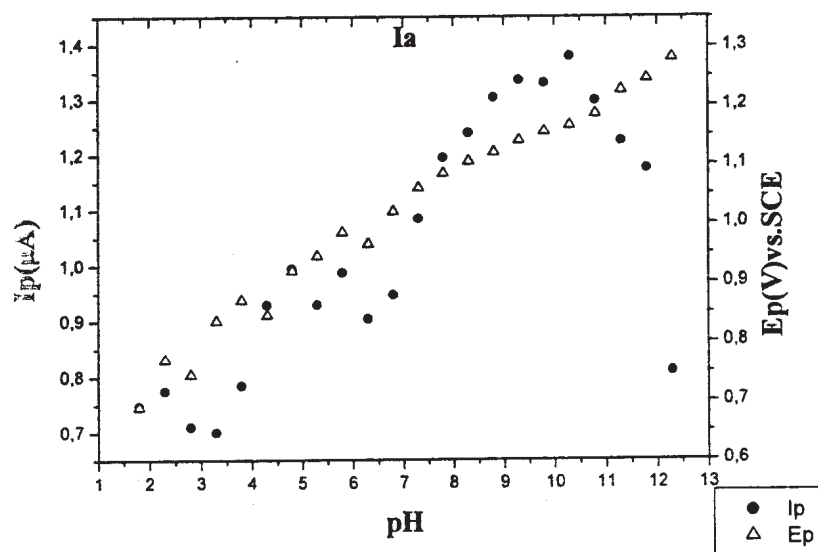


Fig. 2. I_p vs. pH and E_p vs. pH plots for Ia. $v = 0.080$ V/s, $c: 5.080 \times 10^{-5}$ M.

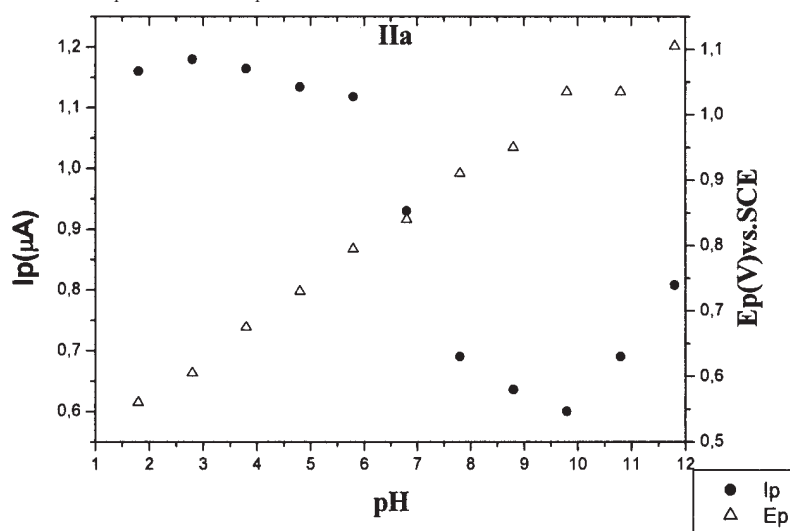


Fig. 3. I_p vs. pH and E_p vs. pH plots for IIa. $v = 0.080$ V/s, $c: 5.488 \times 10^{-5}$ M.

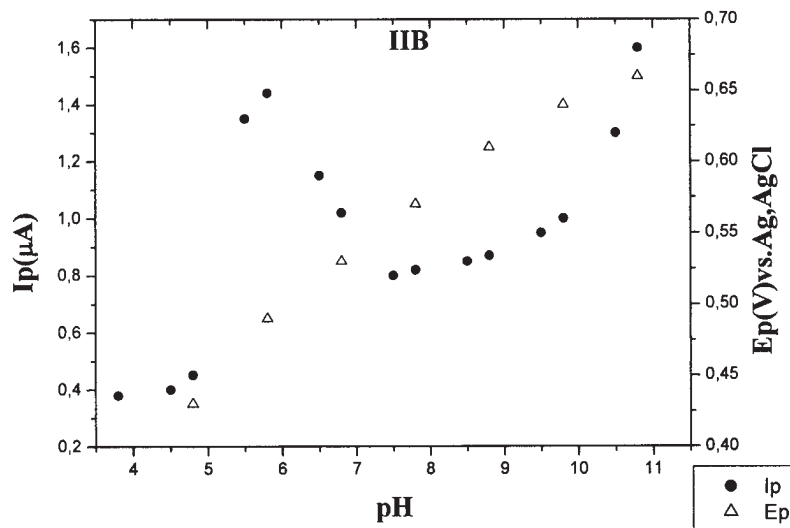


Fig. 4. I_p vs. pH and E_p vs. pH plots for IIB. $\nu = 0.080$ V/s, $c: 5.488 \times 10^{-5}$ M.

The plot of E_p vs. pH showed a straight line in the pH range from 1.80 to 9.80. E_p remained constant between pH 9.80 and 10.80 for both Ia and IIa (Figs. 2 and 3). For fast scan rates (300, 400 mV/s), the plot for Ia showed a break at pH 4.80 in addition to the intersection at pH 9.80. Such a break, however, did not occur for IIa. The E_p values of these peaks were found to be more negative in non-aqueous methanol medium in comparison to those in aqueous methanol that yielded higher currents.

Peak Ia showed a sharp increase in potential between pH 4.30 and 4.80. Such an increase was not observed for IIa. This may indicate intramolecular hydrogen bonding at pH 4.80, and above, between the hydrogen atoms of the unprotonized amino group, NH_2 , and the oxygen atom of the carbonyl group, $>\text{C}=\text{O}$ of **I**. Below pH 4.80, such bonding was not observed since the $-\text{NH}_2$ group was protonated.

Coulometric studies

The coulometric results gave a value of n of 1.54 for Ia and 2.02 for IIa. These findings suggest that the number of electrons transferred corresponding to either Ia and IIa was two. Electrolyses led to disappearance of the following more negative peaks, Ia and IIb. The reduced solutions gave a positive Nessler test¹¹ for ammonia that was performed immediately after completion of the electrolysis. Blank solutions did not show the same result, indicating that ammonia was produced in the reduction processes of compound **I** and **II**.

Each electrolysis yielded chromatographically homogeneous single products. The ultraviolet (UV) absorption maximums at 264 nm obtained for Ia and IIa gradually decreased and shifted to 240 nm upon electrolysis. The shoulders at 320 nm also shifted to 330 nm after electrolysis. These absorption maxima proved that the electrolysis products were stable.

The products from the electrolysis solution were isolated by extracting with diethyl ether and were in the form of a light yellow and a white precipitate for **I** and **II**, respectively. The melting point of the light yellow product was 228 °C (isopropanol) and that for white product was 180 °C (acetic acid). The IR spectra of the reduction products also proved that electrochemical protonation had occurred at the amino group ($-\text{NH}_2$) because of the lack of the primary and secondary amine bands at 3306 and 3175 cm^{-1} (in KBr) obtained in the original IR spectrum of **I**,² and the lack of the amine band at 3242 cm^{-1} (in KBr) obtained in the original IR spectrum of **II**.³

The electrolysis solutions of both compounds were divided into two equal portions in order to further verify whether the elimination of the amino group was due to an electrochemical process. One portion electrolyzed as mentioned above and the second was stored for three days without electrolysis. After three days, the Nessler test for ammonia was negative for the non-electrolyzed portion. In addition, the primary and secondary amine absorption bands were still remaining in the IR spectrum, verifying the fact that the elimination of the amino group was an electrochemical process.

These results demonstrate that peaks Ia and IIa arise from the electrochemical deamination of compound **I** and **II**. For both compounds, the amino groups were in the partially protonated form $-\text{NH}_3^+$ in the acidic solution, therefore the deamination reaction consumed one H^+ and 2e^- for the already protonated species. In the acidic solution and at relatively high pH values, it consumed 2H^+ and 2e^- for the unprotonated species. The reactions associated with these electrode processes are given below:



Based on these reactions, it is clear that the amino molecules were deaminated by scission of protonated and unprotonated $>\text{N}-\text{NH}_2$ bonds of each compound, resulting in the formation of ammonia. This indicated that the pK values for both Ia and IIa were 9.80 from the E_p vs. pH plots given in Figs. 2 and 3, respectively, since the amino group at position 1- was deaminated and the nitrogen atom left at the same position was protonated. The pK values were 10.80 for Ia and 7.80 for IIa, in non-aqueous methanol medium.

Peak Ib and IIb: These peaks were observed best in the pH range between 1.80 and 4.80 and they disappeared at pH 7.80 and above. In the case of compound **II**, neither IIb nor IIc was observed in the non-aqueous methanol medium.

The E_p vs. pH plot showed two linear segments with a breakpoint at pH 4.80 for Ib (it was also obtained for Ia at faster scan rates, *i.e.*, 300 and 400 mV/s) and at pH 5.50 for IIb. The respective equations for $E_p = f(\text{pH})$ variations are summarized

in Table I. The decrease in the slopes for both peaks indicated that the reduced form was an acid.³⁰

TABLE I. Voltametric data. Concentration of compound **I**: 5.080×10^{-5} M, and of compound **II**: 5.488×10^{-5} M, scanning rate, ν : 0.080 V/s.

Peak name	pH Range	Slope	R ²	$E_p/V(\text{SCE})$	Deamination constant	pK_a
Ia	1.80–9.80	–0.059	0.963	0.730/1.155	9.80	–
IIa	1.80–9.80	–0.059	0.999	0.625/1.060	9.80	–
Ib	1.80–4.80	–0.085	0.999	0.805/0.970	–	4.80
	4.80–7.80	–0.054	0.998	0.970/1.120	–	
IIb	2.50–5.50	–0.073	0.999	0.755/0.960	–	5.50
	5.50–7.80	–0.039	0.997	0.960/1.055	–	
Id	1.80–4.80	–0.081	0.998	1.025/1.220	–	–
	4.80–8.30	–0.049	0.998	1.220/1.325	–	
If	1.80–10.80	Independent	–	1.025/1.405	–	–

The breakpoints shifted to pH 5.80 for both Ib and IIb in the non-aqueous methanol medium. The I_p values of these peaks were found to be directly dependent on the potential sweep rate (ν), indicating adsorption. The increase in the value of I_p , however, was less rapid than the square-root of the potential sweep rate. This could be due to the fact that the reactant was probably supplied by a preceding chemical reaction.³¹

These peaks were found to arise from a chemical reaction in which previously unprotonated amino groups, $-\text{NH}_2$ were protonated by the acid or water molecules that existed in the medium. Thus, the breakpoints at pH 4.80 for Ib and of 5.50 for IIb, obtained from the their E_p vs. pH plots, were found to be the acidity constants, (pK_a) of the amino group of each compound.

Peaks arising from the carbonyl and thiocarbonyl group of the compounds

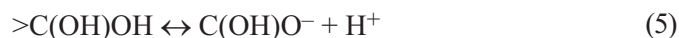
Peak I_d arises from the carbonyl group of I: The occurrence of peak I_d for compound **I** and the absence of II_d for compound **II** indicate that I_d is related to the carbonyl group, $>\text{C}=\text{O}$, at position 2– of compound **I**. Peak I_d was quite small until pH 2.80. It became a well defined peak with increasing pH up to pH 7.80, and L-shaped between pH 7.80 and 9.30. The magnitude of I_d was the same as that of I_a at pH 4.80 and above. In non-aqueous methanol medium, I_d was observed only poorly until pH 4.80, and as a well defined peak in the pH range from 4.80 to 8.80. The peak broadened above pH 8.80. The peak was also observed at more negative potential in non-aqueous methanol compared to those observed in aqueous methanol.

A plot of E_p vs. pH for I_d showed two breakpoints at pH 4.80 and 8.30. This be-

havior was similar to that obtained at faster scan rates for Ia. The respective equations for $E_p = f(\text{pH})$ variations are summarized in Table I. E_p was observed to be independent of pH at higher pH values. In non-aqueous methanol medium, the break-points shifted to pH 5.80 and 8.80. From the equation given in (1), the values of P was calculated to be 1.87 and 0.95 for pH values below and above 4.80, respectively. As for Ia, I_p for Id showed an increase until pH 10.30 and then decrease. These similarities were attributed to the effect of the carbonyl group such that the previously hydrated carbonyl group was dehydrated and the nitrogen atom at position 1- protonized as the pH increased. The current initially increased owing to an increase in the dehydration rate, but then decreased as the solution became more alkaline owing to a decrease in the protonation rate of the nitrogen atom. The carbonyl groups were thought to be hydrated in acidic solutions according to the reaction given below, and the resulting product was not electrochemically reduced:^{30,32,33}



This is an acid-base catalyzed reaction. Hydroxyl ions and other bases catalytically accelerate the dehydration process. The increase in the current of Id up to pH 10.30 confirmed the base catalysis of the dehydration process of the hydrated form according to reaction (5) given below. Such a finding indicates that the current for Id was probably governed by the dehydration rate of the hydrated form:^{30,33}



Peaks IIA, IIB, IIC and IIE, arise from the thiocarbonyl group, $>\text{C}=\text{S}$ of IIA: Peaks IIA, IIB, IIC and IIE were observed only for compound **II**, but not for compound **I**. this result was attributed to the thiocarbonyl group of **II** which also agrees with previous reports.³⁴ The occurrence of peaks IIA and IIB at more positive potentials compared to IIA indicates that the thiocarbonyl group has a greater affinity for mercury than the nitrogen atom in the amino group.

Peaks IIA and IIB were observed as very weak signals on the voltammograms at pH 2.30. With increasing pH, the heights of both peaks increased and at pH values above 8.80 the height of IIA gradually decrease whereas that of IIB increased. IIA was accompanied by a pre-peak which was practically pH dependent. This pre-peak was attributed to the adsorption of the reactant involved in the electrode process.³⁵ At pH values around 11.80, IIA disappeared and IIB reached its maximum height. The peak currents of these peaks were found to increase with increasing sweep rate.

Peak IIA: If the potential sweep was delayed after the working electrode had been places in its comprtment in the cell, the E_p values of peak IIA shifted to more negative potentials. Further, the length of the delay led to increasing I_p values of this peak. The I_p increased with increasing concentration between 4.568×10^{-5} and 5.488×10^{-5} M, and diminished with further increase in the concentration. I_p also

increased with increasing pH up to 8.00 and then decreased. It was found to be directly proportional to the potential sweep rate, v .

The peak potential of peak IIA shifted to more negative potentials with increasing pH, compound concentration and sweep rate in both aqueous and non-aqueous methanol. The E_p vs. pH plot showed two linear segments with a breakpoint at a pH of about 7.80. The relevant equations for $E_p = f(\text{pH})$ variations are summarized in Table II. In non-aqueous methanol medium, the break occurred at pH 8.80. The peak was observed at potentials of approximately 20 mV more positive with higher currents compared to those observed in aqueous methanol. These findings indicate that peak IIA is an adsorption peak originating from the adsorption of unreacted =S molecules on the electrode surface.^{32,34–38} The breakpoint obtained at pH 7.80 was considered to be the pK value for the adsorbed =S species.

TABLE II. Voltammetric data. Concentration of compound I: 5.080×10^{-5} M, and of compound II: 5.488×10^{-5} M, scanning rate, v : 0.080 V/s

Peak name	pH Range	Slope	R^2	$E_p/V(\text{SCE})$	pK_a	$pK_{(\text{proton gained})}$	$pK_{(\text{proton lost})}$
IIA	6.50–7.80	–0.058	0.989	0.170/0.240	7.80	–	–
	7.80–8.80	–0.118	0.969	0.240/0.365			
IIB	4.50–5.80	–0.059	–	0.485/0.530	–	5.80	9.80
	5.80–9.80	–0.038	0.999	0.530/0.650			
IIC	7.50–8.80	–0.032	0.994	0.115/0.160	–	–	–
IIE	5.80–9.80	independent	–	1.120/1.210	–	–	–
IIF	2.50–9.80	independent	–	1.390/1.400	–	–	–

Peak IIB was not a diffusion-controlled peak. The peak current, I_p , increased faster than the square-root of the potential sweep rate. Fig. 4 shows I_p vs. pH and E_p vs. pH plots for this peak. There were two breakpoints at pH 5.80 and 9.80. The individual equations for $E_p = f(\text{pH})$ are summarized in Table II. The slope of the plots passing over the first and second breakpoints diminished with pH. This indicates that the reduced form is an acid.³⁰ The breakpoints in Fig. 4 were found to be shifted to higher pH values (*i.e.*, 6.80 and 10.80) in the non-aqueous methanol medium.

The value of αn_a was computed from the voltammograms²⁷ using $E_p - \ln v$ and was found to be 1.590 for the pH range from 3.80 to 10.80. The value of p was 2.02 for pH values below 5.80, 1.59 for pH values between 5.80 and 9.80, and 0.54 for pH values above 9.80. Generally, the height of IIB was approximately equal to that of IIA indicating the consumption of $2H^+$ and $2e^-$ in the relevant electrode processes.

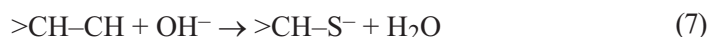
Figure 4 shows that the I_p of IIB reached its maximum height at pH 5.80. Following a subsequent decrease, the peak height showed another increase with in-

creasing pH, starting from a pH of 9.80. This kind of behavior has been observed for the reduction of a mono anion of a dibasic acid.³⁹ A similar relationship between pH and I_p was also seen in the non-aqueous methanol medium. From these findings it was considered that peak IIB resulted from the reduction of one of the $>C=S$ bonds, leading to the formation of a thiol group, $-SH$. The reduction process consuming $2H^+$ and $2e^-$ is given below:



The thiol formed during this reduction behaves as an electroinactive group at the potential of this peak, during the electrode process. The decrease in the current observed at pH values above 5.80 confirms this view and agrees well with reported literature.^{32,38}

This value is approximately equal to the value of 5.85, the first acidity constant of hydrogen sulfide, H_2S .⁴⁰ Therefore, it can be concluded that the first breakpoint is due to the protonation of the sulfur in the thiocarbonyl group. Moreover, this finding suggests that the thiocarbonyl group was in the form of thiol, $-SH$ at pH 5.80. Because the thiol form was dominant in the medium above pH 5.80, it was hydrolysed *via* a base catalyzed hydrolysis reaction in the basic region. The probable reaction which took place is given below:



Above pH 9.80, the thiocarbonyl group was in the form of sulfur ($-S^-$) ions in the medium. Sulfur ions react with any acid to form $-SH$.³² In conclusion, the first and second breakpoints obtained at pH 5.80 and 9.80 were basic pK (proton gained) and the acidic pK (proton lost) values, respectively, related to the thiocarbonyl group of II. In non-aqueous methanol, the basic pK shifted to 6.80 whereas the acidic pK remained constant (pH 9.80). The pH values of 9.80 agrees well with the literature.³³

A weak tautomerization was observed between IIA and IIB in the aqueous methanol medium, but it was more pronounced in the non-aqueous methanol medium. This was attributed to the presence of two forms (the thion form, $=S$ active with IIA and the thiol form, $-SH$ active with IIB) in equilibrium as given below:^{32,34,36-38}



Tautomeric forms of these kinds of compounds are thought to occur in organic solvents⁴⁰ which supports the observation of higher levels of tautomerization in non-aqueous methanol.

Peak IIC: This peak was observed over the narrow pH range from pH 7.50 to 8.80 in aqueous methanol at a potential of about -150 mV. In non-aqueous methanol, it was observed between pH 8.80 and 11.80. The respective equations for $E_p =$

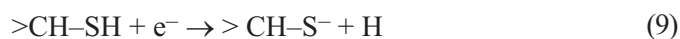
$f(\text{pH})$ variations are summarized in Table II. In aqueous methanol, peak IIC was best seen at pH 8.80 when the E_p was about the same in both media. With increasing sweep rate, the peak potential of IIC shifted to more positive potentials.

In aqueous methanol, the peak current increased with increasing potential sweep rate. However, the current measured in non-aqueous methanol was about twice that measured in aqueous methanol. Since the value of I_p for IIB / I_p for IIC changes with the square root of the potential sweep rate, $v^{1/2}$, a coupled chemical reaction is indicated.³¹ The formation of a compound between the mercury on the electrode surface and the thiol group is very likely to occur in this case.

Catalytic peaks

Peak Iie: A careful examination of the voltammograms revealed a relation between Iie and IIB. Both peaks appeared as very small peaks below pH 5.80 and became more pronounced above pH 6.80. The peak Iie broadened at pH 8.50 and then became L-shaped with increasing pH. The height of the peak was the same as that of IIB, but half of the height of peak Iia. This probably indicates that it arises from a reaction consuming $1e^-$. The height of the peak increased more rapidly as the potential sweep rate increased. As can be seen from the voltammograms given in Fig. 1, peak, Iie appeared at more negative potential than those of IIB by approximately 600 mV. It displayed similar behavior both in non-aqueous methanol and aqueous methanol medium. In non-aqueous methanol, the peak became more pronounced at a pH values of 6.80 and L-shaped above pH 8.80.

The I_p values of peak Iie showed a tendency of increasing up to pH 6.80 and then decreased with further increase in the pH. The E_p values were found to be independent of pH in the pH range between 5.80 and 9.80, the value of E_p could not be calculated because of the merging with peak Iic. These data indicate that peak Iie is a catalytic hydrogen discharge peak that arises from the electrochemical reaction given below taking place at the potential of this peak:³²



The resulting $-S^-$ ions react with any acid to reform $-SH$ which again undergoes the electrochemical reaction given in 9 and so this process occurs continuously. Many sulfur containing organic compounds possess a marked ability for producing such catalytic peaks.¹³

Peaks If and Iif: These peaks were observed at the most negative potentials with much higher currents than the other peaks. If had higher catalytic currents than Iif. The peak currents of these peaks decreased sharply with increasing pH and became nearly zero at pH around 12.00 for If and 7.00 for Iif. These observations are characteristic features of catalytic hydrogen discharge peaks.^{12,32,36,41} Many nitrogen¹² containing organic compounds possess a tendency for producing such peaks as a result of the protonated base being easier to reduce than the proton

itself. Thus these peaks were attributed to catalytic hydrogen discharge peaks originating from the catalytic discharge of the nitrogen atom at position 3- in the pyrimidine ring of both compounds.^{12,37} The reactions for the hydrogen discharge currents are given below:⁴²



The I_p values of these peaks increase as the concentrations of the compounds increased. On the other hand, the E_p values remained constant when the pH and the potential sweep rate were increased. In non-aqueous methanol, these peaks were observed at the most negative potentials and exhibited very small currents with respect to the other peaks.

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ИЗВОД

ЕЛЕКТРОХЕМИЈСКО ПОНАШАЊЕ НЕКИХ НОВИХ ДЕРИВАТА ПИРИМИДИНА

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Испитивана је електрохемијска редукција недавно синтетисана два једињења пири-
мидина, 1-амино-5-бензоил-4-фенил-1Н-пиримидине-2-она (**I**) и 1-амино-5-бензоил-4-фе-
нил-1Н-пиримидин-2-тиона (**II**) цикличном волтаметријом на viseћој живиној капи у
воденом раствору метанола (36 % v/v) и у безводном метанолу. За једињење **I** добијен
је низ катодних максимума без одговарајућих анодних. Са повећањем pH раствора неки
од катодних максимума су се преклапали уз нестанак раније опажених максимума. Код
једињења **II** поред максимума опажених код **I** добивена су и три нова катодна и један
анодни максимум. Повећањем pH потенцијали максимума померали су се у негативном
смеру. Овај померај мерен је у опсегу pH 1,80 – 12,30 рад идређивања pK_a вредности ових
једињења. Константе киселости амино група су 4,80 за једињење **I** и 9,80 за једињење **II**.
Код једињења **II** запажена је тиол-тион таутомеризација која је била израженија у
неводеној метанолској средини. Одређене су pK вредности протонације и депротона-
ције тиокарбонилне групе. Ове pK вредности су 5,80 и 9,80 за водени раствор метанола,
а 6,80 и 10,80 за неводени метанол.

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REFERENCES

1. D. T. Hurst, *The Chemistry and Biochemistry of Pyrimidines, Purines and Pteridines*, Wiley, New York, 1980
2. Y. Akçamur, B. Altural, E. Saripinar, G. Kollenz, O. Kappe, *J. Heterocyclic Chem.* **25** (1988) 1419
3. B. Altural, Y. Akçamur, E. Saripinar, I. Yildirim, G. Kollenz, *Monatshefte für Chemie* **120** (1989) 1015

4. M. S. Motawia, A. E. S. Abdelmegied, E. B. Pederson, C. M. Nielsen, P. Ebbesen, *Acta Chem. Scandinavica* **46** (1992) 77
5. M. C. Correia dos Santos, P. M. P. Sousa, A. M. M. Modesto, M. L. S. Goncalves, *Bioelectrochem. and Bioenergetics* **45** (1998) 267
6. A. K. Jain, S. M. Sondhi, V. K. Sharma, *Electroanalysis* **12** (2000) 301
7. A. Abbaspour, S. M. M. Moosavi, *Talanta* **56** (2002) 91
8. H. S. Seleem, B. A. El-Shetary, S. M. E. Khalil, M. Shebl, *J. Serb. Chem. Soc.* **68** (2003) 729
9. A. Safavi, N. Maleki, E. Shams, H. R. Shahbaazi, *Electroanalysis* **14** (2002) 929
10. P. A. M. Farias, A. L. R. Wagener, M. B. R. Bastos, A. T. da Silva, A. A. Castro, *Talanta* **61** (2003) 829
11. D. L. Smith, P. J. Elving, *J. Am. Chem. Soc.* **84** (1962) 2741
12. P. J. Elving, S. J. Pace, J. E. O'Reilly, *J. Am. Chem. Soc.* **95** (1973) 647
13. M. Wrona, *J. Electroanal. Chem.* **104** (1979) 243
14. A. Izquierdo, E. Bosch, M. D. Prat, *Electrochim. Acta* **27** (1982) 1465
15. J. J. Berzas, J. Rodriguez, J. M. Lemus, G. Castaneda, *Electroanalysis* **7** (1995) 1156
16. B. Z. Zeng, F. Y. Ma, W. C. Purdy, *Electroanalysis* **10** (1998) 677
17. J. L. Yan, R. D. Sun, W. D. Sun, *Chinese J. Analytical Chem.* **31** (2003) 448
18. R. N. Goyal, A. Rastogi, A. Sangal, *New Journal of Chemistry* **25** (2001) 545
19. B. M. Marco, B. L. Ruiz, *Talanta* **61** (2003) 733
20. J. M. F. Alvarez, M. R. Smyth, *Analyst* **114** (1989) 1603
21. P. Bartak, D. Pěchová, P. Tarkowski, P. Bendár, M. Kotouček, Z. Stránský, R. Vespalec, *Anal. Chim. Acta.* **421** (2000) 221
22. R. Battistuzzi, M. Borsari, D. Dallari, G. Gavioli, C. Tavagnacco, G. Costa, *J. Electroanal. Chem.* **368** (1994) 227
23. A. M. A. Helmy, M. A. Migahed, M. A. Morsi, *J. Electroanal. Chem.* **388** (1995) 109
24. F. Rived, M. Rosés, E. Bosch, *Anal. Chim. Acta* **374** (1998) 309
25. M. E. Hanke, M. Johnson, *Science* **78** (2027) (1933) 414
26. D. D. Perrin, B. Dempsey, *Buffers for pH and Metal Ion Control*, Chapman and Hall, 1974
27. A. J. Bard, L. R. Faulkner, *Electrochemical Methods, Fundamentals and Applications*, Wiley, New York, 1988
28. J. J. Lingane, *J. Am. Chem. Soc.* **67** (1945) 1916
29. J. Heyrovski, J. Kuta, *Principles of Polarography*, Czechoslovak Academy of Sciences, Prague, 1968
30. A. P. Tomilov, S. G. Mairanovskii, M. Ya. Fioshin, V. A. Smirnov, *Electrochemistry of Organic Compounds*, Halsted Press, New York, 1972
31. D. Pletcher, *Advanced Instrumental Methods in Electrode Kinetics*, Lecture Notes For The Southampton Course, The Department of Chem., The University of Southampton, 1975
32. I. M. Kolthoff, J. J. Lingane, *Polarography*, Second Ed. Vol. II, Interscience, New York, 1955
33. P. Zuman, *Microchemical J.* **57** (1997) 4
34. P. Zuman, *Topics in Organic Polarography*, Plenum Press, New York, 1970
35. M. R. Smyth, J. G. Osteryoung, *Anal. Chem.* **50** (1978) 1632
36. T. Selzer, Z. Rappoport, *J. Org. Chem.* **61** (1996) 5462
37. J. Bukowska, K. Jackowska, *J. Electroanal. Chem.* **367** (1994) 41
38. B. E. Conway, J. O'M. Bockris, E. Yeager, S.U.M. Khan, R. White, *Comprehensive Treatise of Electrochem.*, Vol. 7, Plenum Press, New York, 1983
39. P. Zuman, *The Use of Polarography in the Initial Stages of Investigations of Mechanisms of Organic Electrode Processes in Aqueous Solutions*. Based on a lecture given on April 28, (1998) at the Department of Analytical Chemistry of the Faculty of Chemical Technology at Pardubice
40. I. M. Kolthoff, E. B. Sandell, E. J. Meehan, S. Bruckenstein, *Quantitative Chemical Analysis*, The Macmillan Company, New York, 1969
41. B. Janik, P. J. Elving, *Chem. Rev.* **68** (1968) 295
42. P. J. Elving, *J. Am. Chem. Soc.* **95** (1973) 658.