

Electrochemical Synthesis of Pyrazine-2,3-Dicarboxylic Acid. Studies Carried Out Using Cyclic Voltammetry on a Stainless Steel Electrode

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Abstract: The studies show the regeneration process of KMnO_4 on stainless steel electrode, comparative with the ones obtained on platinum electrode. The studies were made through cyclic voltammetry at concentrations of support electrolyte (KOH) of about 5 to 10%, at 25-40°C temperature, KMnO_4 concentration until $6 \cdot 10^{-2}$ M and maximum concentration of quinoxaline until $2.61 \cdot 10^{-2}$ M, in electrolyte solution. It seems that on stainless steel electrode is not possible to do the oxidation of Mn^{6+} to Mn^{7+} like on platinum [1,2], nickel [3] or copper electrode [4]. However, a final decision will be made after the effectuation of new investigations (preliminary synthesis).

Keywords: electrochemistry, cyclic voltammetry, quinoxaline, pyrazine-2,3-dicarboxylic acid, stainless steel electrode

1. Introduction

Due to the simplicity in manufacturing and of the low price, after the studies carried out using platinum [1,2], nickel [3] and copper [4] electrodes, we focused on studying the possibility of using stainless steel electrode in the process of Mn^{7+} regeneration. The Mn^{7+} ions can be used in the process of chemical oxidation of quinoxaline in order to obtain pyrazine-2,3-dicarboxylic acid. Because one of the most suggestive results were obtained by means of platinum electrode, we compared all the results of the stainless steel electrode with the results obtained using a platinum electrode.

2. Experimental

In order to carry out the studies we used the same cell of electrolysis used before [1,2,3,4] equipped with three electrodes – a platinum counter electrode, a reference electrode, ESC, and the working electrodes used for measurements were stainless steel electrode and respectively the platinum electrode. We used a stainless steel wire with a diameter of 0.025 cm^2 . The platinum electrode was made up of a platinum wire with an exterior surface of 0.2 cm^2 . The electrodes were cleaned before each measurement by diving into diluted nitric acid, then into a solution of oxalic acid in 20% sulfuric acid for about 10 minutes. The electrode cleaned this way was used for a series of measurements. Sometimes – when the results demanded – the process of cleaning was repeated.

The conditions of work were the same as those used for the study of the platinum electrode [1,2].

The studies of cyclic voltammetry were carried out using a potentiostat PGZ 301 DynamicsEIS Voltammetry-Radiometry Copenhagen, equipped with VoltaMaster 4 as an operating system. As a support electrolyte we used solutions of 5% and 10% of KOH, at temperatures ranging between 25 and 40°C. The concentration of the potassium

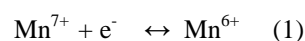
permanganate and quinoxaline (solutions dissolved into KOH of the same concentration used in measurements – 5 and respectively 10%) was 1N and 0.5M respectively. The working intervals used was 0÷+700 mV for both stainless steel and platinum electrode. The speed of polarization was 100 mV/s. Every time, the third voltammogram recorded was kept. All the potentials in this paper are reported to ESC (if is not mentioned otherwise).

3. Results and discussions

Figure 1 presents the curves obtained by cyclic voltammetry at 25°C using a solution of KOH 5% for different concentrations of KMnO_4 on platinum (B), respectively stainless steel (A). The curve 1 is obtained using KOH 5% in the absence of Mn^{7+} . In the given interval no process takes place. The release of the oxygen onto the surface of platinum takes place at a higher potential than 700 mV and the same process on stainless steel takes place over 600 mV.

The increase in Mn^{7+} concentration on platinum leads to the modification of the curves, 3 peaks appear: an anodic peak at 450 mV and two cathodic peaks at about 300 mV and respectively 80 mV. On the platinum when the increase of the Mn^{7+} concentration occurs in the electrolyte, the modification of the curves is observed.

The intensity of the peaks increases with the increase of Mn^{7+} concentration. In the same time the peaks shift toward more negative values (the cathodic peaks), respectively towards more positive values (the anodic peaks). It is clear that on the electrode surface, in the presence of manganese ions several processes take place. From the aspect of the curves we can observe that the anodic peak and the cathodic peak 1 correspond to a reversible process, probably the one illustrated by the reaction below:



The second cathodic peak corresponds to a more advanced reduction of the Mn^{7+} , probably leading to Mn^{4+} .

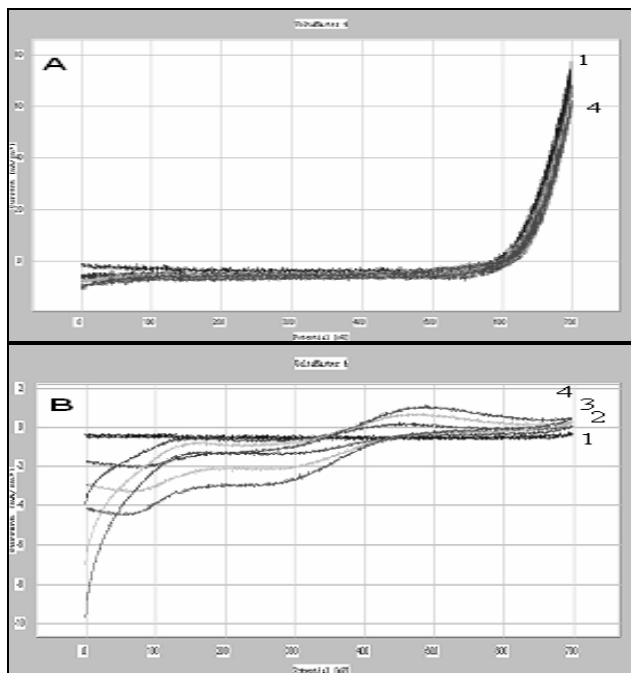


Figure 1. $T = 25\text{ }^{\circ}\text{C}$, sol KOH 5%, concentration of $KMnO_4$: 1 – 0, 2 – $2 \cdot 10^{-2}\text{ M}$, 3 – $3,8 \cdot 10^{-2}\text{ M}$, 4 – $6 \cdot 10^{-2}\text{ M}$, A – stainless steel electrode, B – platinum electrode.

In the absence of the organic substance, the source of Mn^{6+} is the dissociation in basic environment of the Mn^{7+} .

On the stainless steel electrode (curve A, figure 1) the introduction of $KMnO_4$ in the electrolyte, in concentrations of maximum $6 \cdot 10^{-2}\text{ M}$, does not lead to supplementary peaks – so no other process takes place on the electrode than those observed using the platinum electrode.

The oxygen formation slightly shift towards more positive values. It seems that on the stainless steel electrode the regeneration of Mn^{7+} does not take place.

In the presence of quinoxaline the curves presented in figure 2 are obtained.

On platinum (B) the presence of quinoxaline in the electrolyte causes the slight modification of the curves. The peaks corresponding to the reversible process: $Mn^{7+} + e \leftrightarrow Mn^{6+}$ are especially modified. The intensity of the peaks increases with the concentration of Q and even shifts with 10 mV towards more negative values. From those observed in figure 2 it seems that the adding of Q has an effect similar to the effect caused by the increase of Mn^{6+} concentration – the increase of the anodic peak – increase which can be motivated by the increase in the concentration of Mn^{6+} in the electrolyte as a result of the chemical reaction between Mn^{7+} and Q. The second cathodic peak seems to decrease in intensity – effect associated to the decrease of the reduction of Mn^{6+} to Mn^{4+} , process desirable to our process of Mn^{7+} regeneration. As we know, Mn^{4+} cannot be turned to a superior oxidation status (6+ or 7+), because it precipitates in the electrolyte and can be considered lost for the process of Mn^{7+} regeneration. Moreover, its presence has a catalytic effect

for the advanced dissociation of the potassium manganate and permanganate ions, so the forming of the MnO_2 is totally unwanted.

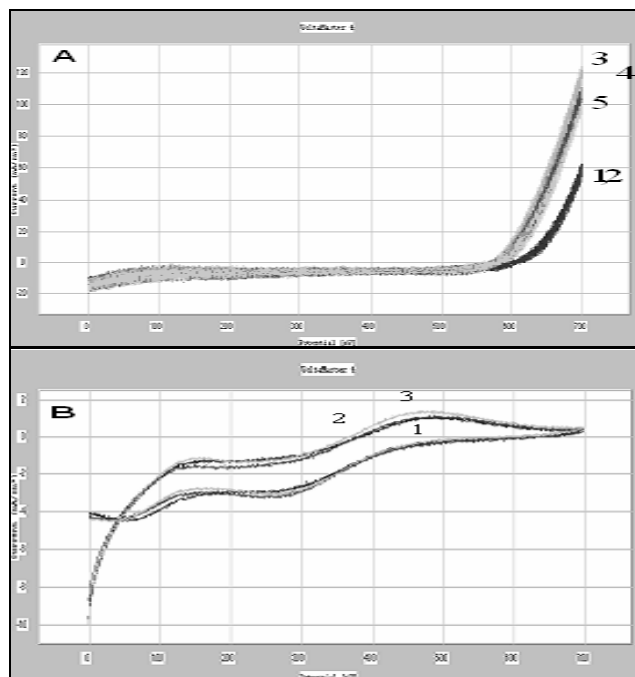


Figure 2. $T = 25\text{ }^{\circ}\text{C}$, sol. KOH 5%, concentration of $KMnO_4$ $6 \cdot 10^{-2}\text{ M}$, conc. of Q: 1 – 0, 2 – $1,18 \cdot 10^{-2}\text{ M}$, 3 – $2,04 \cdot 10^{-2}\text{ M}$, 4 – $2,61 \cdot 10^{-2}\text{ M}$, 5 – $3,62 \cdot 10^{-2}\text{ M}$, A – stainless steel electrode, B – platinum electrode.

As a comparison with platinum, on the stainless steel electrode only a process of shifting the release of oxygen towards more positive values takes place. This process is not proportional with the quantity of Q. The variation is not uniform and can be a result of the absorbance of Q onto the electrode. Though less likely, the direct oxidation of Q on the electrode could take place together with the oxygen release. Anyway, what we want is the regeneration of Mn^{7+} from Mn^{6+} and this process is not to be seen on the curves.

If the experiments are carried out in solution of KOH 5% at $40\text{ }^{\circ}\text{C}$ we obtain the curves presented in figure 3.

On the basic curve, in the absence of potassium permanganate we cannot notice any electrode process in the interval studied (curves 1). On the platinum electrode (B) the adding of potassium permanganate leads once again – as it did at $25\text{ }^{\circ}\text{C}$ (figure 1B) – to the increase of the peaks corresponding to the reversible process (1) and to the accentuation of the cathodic peak corresponding to the reduction of Mn^{4+} . In the moment we add Mn^{7+} in the system we can notice the presence of Mn^{6+} formed by chemical reduction in basic medium. The peaks are better defined than at $25\text{ }^{\circ}\text{C}$ and the increase of temperature causes the increase of the intensity for the peaks, which shows the favorable effect over the electrode process of the increase in temperature of the electrolyte.

At the same composition of the electrolyte, the increase of the temperature has as effect the increase of the intensity of the anodic peak with 30%, while the cathodic peaks suffer a 30% respectively 20% increase.

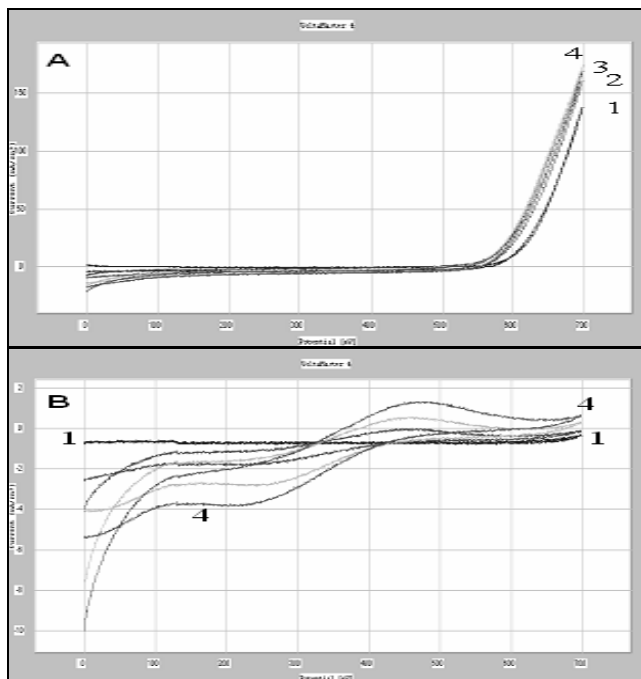


Figure 3. $T = 40^{\circ}\text{C}$, sol. KOH 5%, concentration of KMnO_4 : 1 – 0, 2 – $2 \cdot 10^{-2}\text{M}$, 3 – $3.8 \cdot 10^{-2}\text{M}$, 4 – $6 \cdot 10^{-2}\text{M}$, A – stainless steel electrode, B – platinum electrode.

If the studies are carried out on a stainless steel electrode (A), the increase of the KMnO_4 concentration does not lead to the apparition of any peaks but only the slight shift of the potential for the oxygen release to more negative values. This time the depolarization is proportional to the concentration of Mn^{7+} . Not even at this temperature we cannot obtain proof of the fact that the regeneration of Mn^{7+} would be carried out on the stainless steel electrode.

The presence of Q in the electrolyte is presented in the curves from figure 4.

The presence of Q on the stainless steel electrode (A), at this temperature does not modify the curves. We can observe an accentuated polarization at the highest concentration of Q, $3.62 \cdot 10^{-2}\text{M}$ (figure 4A).

The studies carried out on the platinum electrode in the presence of quinoxaline (B) clearly show the peaks of the reversible process (1) and the peak caused by the reduction of Mn^{4+} . Unlike the situation at 25°C , where the presence of Q had as effect the increase of both the peaks of the reversible process – and the anodic peak at about 480 mV and the cathodic peak at 210 mV – at 40°C we can observe the increase of the anodic peak, proportional with the concentration of Q, but the cathodic peak decreases. This decrease is proportional with the concentration of Q. In the same time, the potential of the anodic peak shifts towards more positive values with the concentration of Q, while the cathodic potential remains practically constant.

The values of the anodic potentials shift toward more positive values than at 25°C and the cathodic shift towards more negative values. This status can be explained by the increase of Mn^{6+} as a result of the increase in the speed of the reaction of Q with Mn^{7+} (with generation of Mn^{6+}) along with the increase of temperature, for the anodic peak.

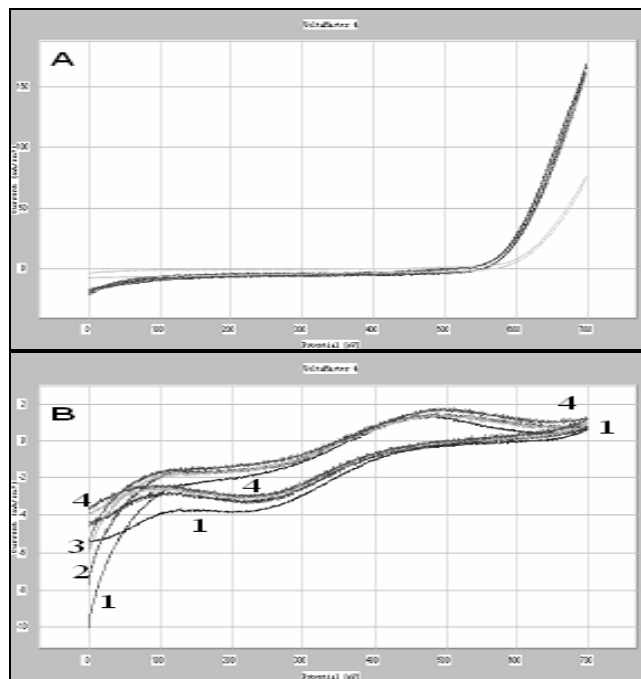


Figure 4. $T = 40^{\circ}\text{C}$, sol. KOH 5%, concentration of KMnO_4 $6 \cdot 10^{-2}\text{M}$, concentration of Q: 1 – 0, 2 – $1.18 \cdot 10^{-2}$, 3 – $2.04 \cdot 10^{-2}$, 4 – $2.61 \cdot 10^{-2}\text{M}$, 5 – $3.62 \cdot 10^{-2}\text{M}$, A – stainless steel electrode, B – platinum electrode.

The decrease of the cathodic peak can be associated with the decrease of Mn^{7+} concentration. On one hand Mn^{7+} is consumed by the Q introduced into the electrolyte (with a higher speed at 40°C) and on the other hand it seems that the regeneration of Mn^{7+} has not a sufficiently high speed.

This would lead to the extinction of Mn^{7+} from the solution of electrolyte and finally to the end of the reaction. We must then give a special attention to this aspect because it seems that temperature has a significant effect towards the process carried out at the electrode.

The increase of the KOH concentration at 10%, at a temperature of 25°C leads to the curves presented in fig. 5.

Neither in KOH 10% on stainless steel the desired peaks do not appear, only a polarization process resulting from the release of oxygen. This polarization is proportional to the concentration of KMnO_4 (A). We cannot notice any modification of the curves obtained in the presence of potassium permanganate. This leads to the conclusion that there are no signs of the regeneration of Mn^{7+} .

On platinum, the presence of potassium permanganate causes the apparition of 4 peaks – two anodic and two cathodic. We can notice the presence of the two peaks characteristic to the reversible process (1) – the anodic peak at 450 mV and the cathodic peak at 320 mV. The peaks increase with the concentration of Mn^{7+} , are better defined than in KOH 5% and are shifted towards more negative potentials the anodic one and towards more positive potentials the cathodic one. We can observe thus a closeness of the two peaks, a better definition of every peak and even of the reversible process in comparison to the reactions carried out in KOH 5%. The release of oxygen shifts towards more negative values along the increase of KMnO_4 concentration.

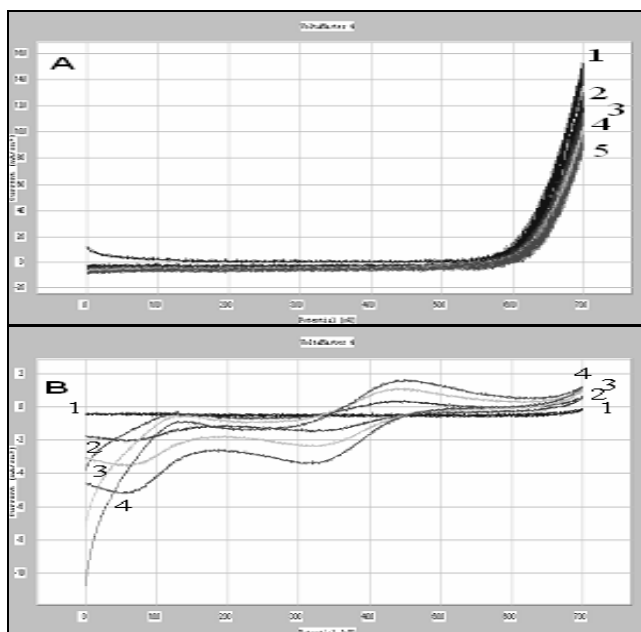


Figure 5. $T = 25\text{ }^{\circ}\text{C}$, sol. KOH 10%, concentration of KMnO_4 : 1 – 0, 2 – $2 \cdot 10^{-2}$ M, 3 – $3.8 \cdot 10^{-2}$ M, 4 – $6 \cdot 10^{-2}$ M, A – stainless steel electrode, B – platinum electrode.

A similar evolution can be observed at the other two peaks. The cathodic peak – present for KOH 5% – is with about 1 mA/cm^2 greater than for KOH 10%, is slightly shifted towards more negative values and is probably associated with the reduction of Mn^{4+} . A special remark must be done for the second anodic peak, at 120 mV. Though small in intensity this peak is well defined, especially at greater concentrations. This peak is not present in KOH 5%. The process which can be associated to this peak is probably the oxidation of Mn^{2+} .

It is obvious that with the increase in KOH concentration to 10% in the electrolyte the peaks associated to the electrode processes increase in intensity and are better defined than in KOH 5% for the platinum electrode while for the stainless steel electrode no other peak can be observed.

In the presence of Q in KOH 10% the next curves can be obtained (figure 6):

In figure 6 A the curves are obtained using a stainless steel electrode in the presence of Q, showing the same situation as for the KOH 5%, a not uniform evolution but with trends of polarization of the oxygen release. Still we cannot notice any signs of transformation of the manganate ions.

The studies carried out on a platinum electrode using an important amount of quinoxaline in electrolyte, lead to the results presented in figure 6 B. The increase of the Q concentration has no other significant effects on the curves. The anodic peak at 440 mV increases very easily, while the associated cathodic peak decreases slightly. These observations are suitable for the peaks around 100 mV. In these conditions it seems that the processes associated to these peaks are reversible.

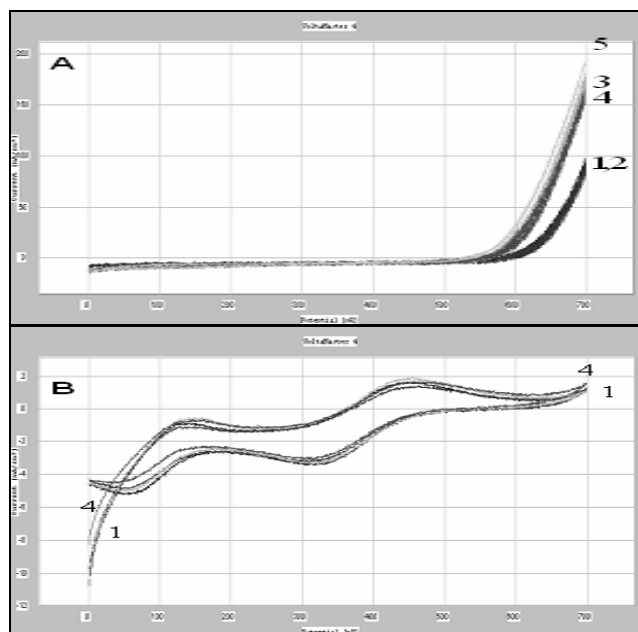


Figure 6. $T = 25\text{ }^{\circ}\text{C}$, sol. KOH 10%, concentration of KMnO_4 $6 \cdot 10^{-2}$ M, concentration of Q: 1 – 0, 2 – $1.18 \cdot 10^{-2}$, 3 – $2.04 \cdot 10^{-2}$, 4 – $2.61 \cdot 10^{-2}$, 5 – $3.62 \cdot 10^{-2}$ M, A – stainless steel electrode, B – platinum electrode.

In this case, the cathodic peak decreases in intensity with the increase of Q concentration while the anodic peak has a slight trend of increase. Anyway, the differences between the curves are not very big yet the trend seems that presented above. On the platinum electrode we can achieve the regeneration of Mn^{7+} in KOH 10% at 25° .

The increase of KOH concentration in the support electrolyte has as effect the accentuation of the peaks observed and a better definition of the electrode processes which leads to positive effects on the desired reaction of Mn^{7+} regeneration.

The curves obtained at 40°C , with KMnO_4 supplementary added are shown in figure 7.

On the curves recorded for the stainless steel electrode there is no process, except the release of oxygen. It is pretty clear that on the stainless steel electrode there is no process of oxidation of Mn^{6+} to Mn^{7+} so that not even at 40°C in KOH 10% the regeneration of Mn^{7+} used for the chemical oxidation of Q resulting in pyrazine-2,3-dicarboxylic acid is not possible.

On the platinum electrode, at 40°C in KOH 10%, the aspect of the curves is the one described above; we can notice the same two anodic peaks – at about 440 mV and one at about 110 mV, rather weak, and visible only at greater concentrations – and two cathodic peaks at 310 and respectively 40 mV. The processes associated to these peaks are those mentioned. We should also mention that the intensity of the cathodic peaks is greater at 25°C in KOH 10% demonstrating the favourable effect of the temperature over the electrode reactions.

In presence of Q at 40°C and in KOH 10% we can obtain the curves presented in figure 8.

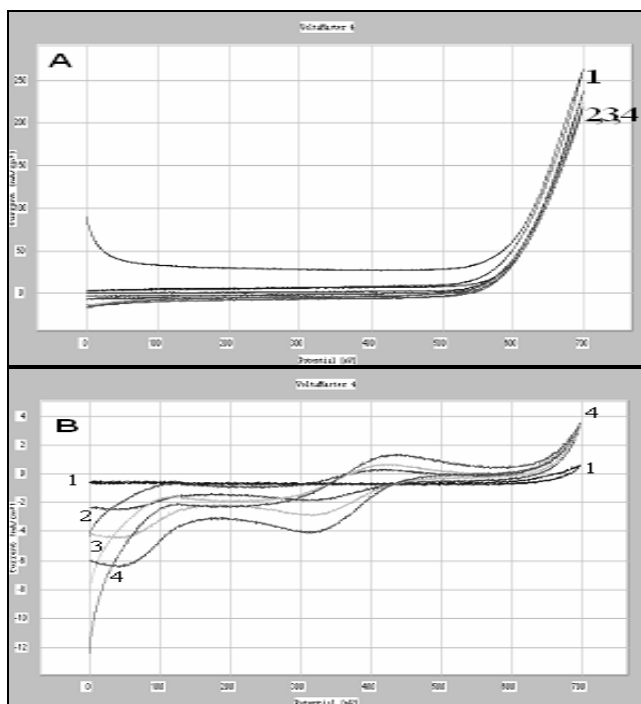


Figure 7. $T = 40\text{ }^{\circ}\text{C}$, sol. KOH 10%, concentration of KMnO_4 : 1 – 0, 2 – $2 \cdot 10^{-2}\text{ M}$, 3 – $3.8 \cdot 10^{-2}\text{ M}$, 4 – $6 \cdot 10^{-2}\text{ M}$, A – stainless steel electrode, B – platinum electrode.

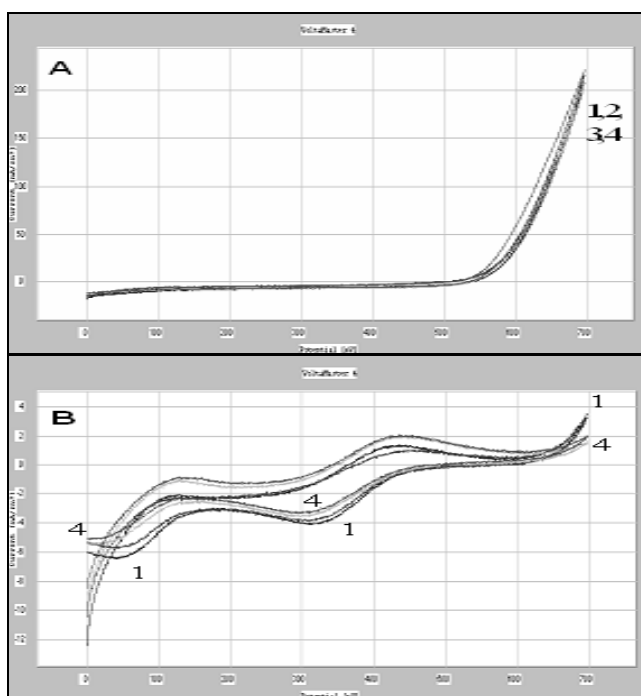


Figure 8. $T = 40\text{ }^{\circ}\text{C}$, sol. KOH 10%, concentration of KMnO_4 $6 \cdot 10^{-2}\text{ M}$, concentration of Q: 1 – 0, 2 – $1.18 \cdot 10^{-2}$, 3 – $2.04 \cdot 10^{-2}$, 4 – $2.61 \cdot 10^{-2}\text{ M}$, A – stainless steel electrode, B – platinum electrode.

If on the stainless steel electrode (A) we cannot notice any modification of the cyclic voltammograms obtained on the platinum electrode, as an increase of the Q concentration the 4 peaks observed modify by the following:

- the first anodic peak, from about 130 mV is slightly shifted towards more positive values than the situation without Q;
- the anodic peak from 440 mV increases in intensity with the concentration of Q – proving the increase of Mn^{6+} with Q;
- both cathodic peaks decrease in intensity with the increase in Q;
- the decrease is more visible for the cathodic peak from 50 mV.

Along the increase of Q concentration we can observe a polarization process of oxygen release, process happening only when Q is added into the electrolyte. The gradual adding of Mn^{7+} has as effect a depolarization of the oxygen emanation.

4. Conclusions

From the studies carried out on the oxidation process of Mn^{6+} to Mn^{7+} on the platinum and stainless steel electrodes by cyclic voltammetry, for the regeneration of the potassium permanganate which can be used for the oxidation of quinoxaline to pyrazine-2,3-dicarboxylic acid we can sum up that the process takes place very well on a platinum electrode and almost it does not take place on the stainless steel electrode.

On the platinum electrode the reversible process $\text{Mn}^{7+} + \text{e}^- \leftrightarrow \text{Mn}^{6+}$, is illustrated. This process takes place at 450 mV for the oxidation and 300 mV for the reduction. The process of anodic regeneration of Mn^{7+} on the platinum electrode is promoted by the increase of:

- the concentration of KOH;
- the temperature;
- the concentration of Mn^{7+} (and Mn^{6+});
- the quinoxaline concentration.

The stainless steel electrode shows slight polarizations or depolarisations of the process of oxygen release so that it seems that the oxidation of Mn^{6+} to Mn^{7+} , is not possible. Nevertheless a final decision will be made only after carrying out new investigations (preliminary syntheses).

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