

# Electrochemical Synthesis of the Pyrazine-2,3-Dicarboxylic Acid. Electrochemical Kinetic Studies on Platinum Electrode

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**Abstract:** In this paper are presented the obtained results from studies made through cyclic voltammetry, on platinum electrode, about electrochemical regeneration process of  $\text{KMnO}_4$  with aim to use it in chemical oxidation of quinoxaline and generation of pyrazine-2,3-dicarboxylic acid. It was investigated the effect of the support electrolyte concentration (KOH), concentration of  $\text{K}_2\text{MnO}_4$ , quinoxaline concentration and temperature. Anodic regeneration process of the  $\text{Mn}^{7+}$  is favored by increase of KOH concentration, temperature,  $\text{Mn}^{6+}$  concentration and quinoxaline concentration.

**Keywords:** electrosynthesis, pyrazine-2,3-dicarboxylic acid, platinum electrode, potassium permanganate, cyclic voltammetry.

## 1. Introduction

*Pyrazine-2,3-dicarboxylic acid*, as well as some its derivatives, are useful intermediaries for tuberculostatic remedies synthesis, as regulators in the forming and the proliferation of the cells, as well as in the treatment of other viral, bacterial or fungicidal diseases [1,2]. Among oxidative methods for synthesis the most known and used is the one based on quinoxaline oxidation with an aqueous potassium permanganate solution, with or without sodium hydroxide addition [3,4,5]. The chemical method is laborious and implies a huge consume of potassium permanganate – 1:16M. Whether potassium permanganate regeneration could be made electrochemically then a significant reduction of used reactive became possible ( $\text{Mn}^{7+}$ ) and the increase of the process efficiency.

Ours unpublished studies has proved that electro oxidation of potassium manganate, in KOH solution, on platinum electrode is possible. Potassium permanganate obtained in this way can be successfully used in pyrazine-2,3-dicarboxylic acid obtaining from quinoxaline. This method can save important amounts of reagents and energy.

In this paper are presented the results obtained through cyclic voltammetry regarding the study of  $\text{Mn}^{6+}/\text{Mn}^{7+}$  couple behavior on platinum electrode, in the presence of quinoxaline, as intermediary step in development of a economical electrochemical process to obtain pyrazine-2,3-dicarboxylic acid (PDA).

## 2. Experimental

To realize the studies we used an electrolysis cell confectioned from glass, with cooling/heating mantle, equipped with three electrodes – one platinum counter electrode, one reference SCE electrode and the working electrode also made from platinum. The surface of the used electrodes was, for the counter electrode –  $1\text{cm}^2$  and for the work electrode, platinum wire –  $0.2\text{cm}^2$ . On these

electrodes has been effectuated the studies for regeneration of the potassium permanganate through anodic oxidation of the potassium manganate. The scope was the determination of conditions in which the regeneration of  $\text{Mn}^{7+}$  is made with maximum efficiency at anode in the presence of quinoxaline (Q).

Cyclic voltammetry studies were effectuated utilizing a potentiostat type PGZ 301 DynamicEIS Voltammetry-Radiometer Copenhagen, equipped with VoltaMaster 4 software.

As support electrolyte we used KOH, solution with 5% and 10 % concentrations, at temperatures of 25 and 50 °C. Electrolyte volume used at every determination was 25 ml and concentration of potassium manganate and quinoxaline solutions (solutions in KOH with same concentration with one used in determinations – 5 respectively 10 %) it was of 1N respectively 0.5M. Cyclic voltammetry studies were made in 0 ÷ +700 mV interval. Polarization speed was 100 mV/s. Every time was kept the third traced voltammogram.

The electrode was cleaned before every determination through diving in a solution of oxalic acid in 20 % sulfuric acid – approximate 10 minutes – succeeded of anodic polarization in 20 % sulfuric acid at  $\epsilon = 1\text{V}$  and maintaining at this potential a period of 5 minutes. Hereby treated electrode was utilized in a lot of determinations. Sometimes it was necessary to repeat the treatment.

All the potentials in this study are referred to SCE, if is not specified otherwise.

## 3. Results and discussions

In Fig. 1 are presented the curves obtained through cyclic voltammetry at 25 °C in 5 % KOH solutions at different concentrations of  $\text{K}_2\text{MnO}_4$ . The curve 1 is traced in 5 % KOH solution, in the absence of  $\text{Mn}^{6+}$  ion. In working interval has not developed any process. At a potential over 700 mV is liberated the oxygen.

Increase of  $\text{Mn}^{6+}$  concentration in electrolyte has tendency to modify traced curves. In addition appear 3 peaks, one anodic at a potential of 450 mV and two

cathodic at approximately 300 mV and respectively 80 mV. A fourth peak – the anodic one – is slightly definite, but it can be accentuated at a potential of approximately 150 mV, particularly at increased concentrations of  $Mn^{6+}$ .

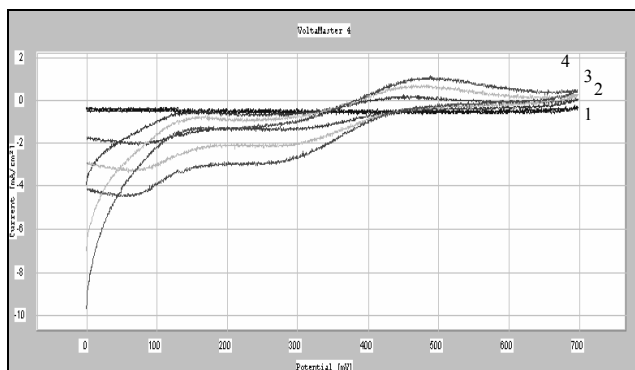


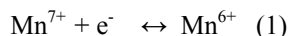
Figure 1. Platinum electrode,  $T = 25\text{ }^{\circ}\text{C}$ ; 5% KOH sol.,  $K_2MnO_4$  concentration: 1 – 0; 2 –  $2 \cdot 10^{-2}$  M; 3 –  $3.8 \cdot 10^{-2}$  M; 4 –  $6 \cdot 10^{-2}$  M.

At the same time with increase of  $Mn^{6+}$  concentration the intensity of peaks increase, same anodic peaks shift to positive values and cathodic peaks shift to negative values. The intensity and potentials of the peaks are presented in Table 1.

TABLE 1 Platinum electrode,  $T = 25\text{ }^{\circ}\text{C}$ ; 5% KOH sol.,  $K_2MnO_4$  concentration: 1 – 0; 2 –  $2 \cdot 10^{-2}$  M; 3 –  $3.8 \cdot 10^{-2}$  M; 4 –  $6 \cdot 10^{-2}$  M.

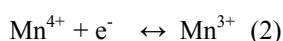
$Mn^{6+}$ electrolyte conc. ( $T = 25\text{ }^{\circ}\text{C}$ )	KOH sol, 5%	$2 \cdot 10^{-2}$ M	$3.8 \cdot 10^{-2}$ M	$6 \cdot 10^{-2}$ M
$\epsilon_{pa}$ [mV]	-	455.18	475.02	491.55
$I_{pa}$ [ $\text{mA}/\text{cm}^2$ ]	-	0.2125	0.6832	1.078
$\epsilon_{pc1}$ [mV]	-	295.56	270.39	248.56
$I_{pc1}$ [ $\text{mA}/\text{cm}^2$ ]	-	-1.3664	-2.1104	-2.954
$\epsilon_{pc2}$ [mV]	-	78.933	65.498	53.742
$I_{pc2}$ [ $\text{mA}/\text{cm}^2$ ]	-	-2.0497	-3.2947	-4.4184

From the aspect of the traced curves we can observe that anodic and cathodic peaks 1 correspond of a reversible process, probably one corresponding to the below reaction.



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

The slightly definite anodic peak corresponds to the reversible corresponding process –  $Mn^{3+}$  oxidation.



The increase of the  $Mn^{6+}$  concentration in electrolyte leads to the increase of all these peaks.

The introduction of quinoxaline (Q) in electrolyte solution led to the curves illustrated in Fig. 2.

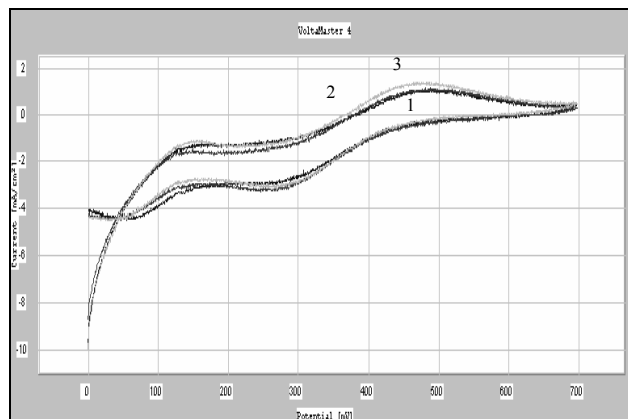


Figure 2. Platinum electrode,  $T = 25\text{ }^{\circ}\text{C}$ ; 5% KOH sol.,  $K_2MnO_4$  concentration is  $6 \cdot 10^{-2}$  M; Q concentration: 1 – 0; 2 –  $1.18 \cdot 10^{-2}$  M; 3 –  $2.04 \cdot 10^{-2}$  M.

The quinoxaline presence into the electrolyte solution produce a slightly modification of the traced curves. Are modified, in special the peaks corresponding to the reversible process  $Mn^{7+} + e^- \leftrightarrow Mn^{6+}$ . The peaks intensity increase slightly with the concentration of Q and actually shift with approximately 10 mV towards negative values. From Fig. 2 seems that the added Q has a similar effect with one of the increase of the  $Mn^{6+}$  concentration – increase of anodic peak – increase which can be justified through chemical reaction between  $Mn^{7+}$  and Q. This is the source responsible for the increase of the  $Mn^{6+}$  concentration in the electrolyte. The second cathodic peak seems to diminish in intensity.

From the observed by now seems that the introduction of  $Mn^{6+}$  conduce at increase of peaks observed in this interval and quinoxaline introduction lead to an increase of reversible process peaks and the diminution of peak associated by us with formation of  $Mn^{4+}$  with approximately 50 mV.

The increase of the electrolyte temperature at  $40\text{ }^{\circ}\text{C}$ , maintaining the other parameters constants, led to curves illustrated in Fig. 3.

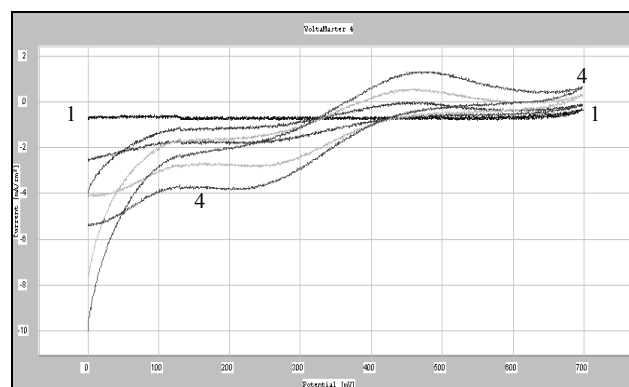


Figure 3. Platinum electrode,  $T = 40\text{ }^{\circ}\text{C}$ ; 5% KOH sol.,  $K_2MnO_4$  concentration: 1 – 0; 2 –  $2 \cdot 10^{-2}$  M; 3 –  $3.8 \cdot 10^{-2}$  M; 4 –  $6 \cdot 10^{-2}$  M.

On the main curve, in the absence of potassium manganate, into the studied interval is not observed any electrode process. Adding potassium manganate lead again – as at  $25\text{ }^{\circ}\text{C}$  – at formation and increase of peaks

corresponding to reversible process (1) and also to increase of cathodic peak appropriate to  $\text{Mn}^{4+}$  reduction. The temperature increase leads at more intense peaks comparable with ones at 25 °C which demonstrate the favorable effect to the electrode process of increasing electrolyte temperature.

At the same composition of electrolyte, increase of temperature leads to increase of anodic peak intensity by 30 % and of cathodic peaks by 30 % respectively 20 %.

The presence of Q into electrolyte leads at curves presented in Fig. 4.

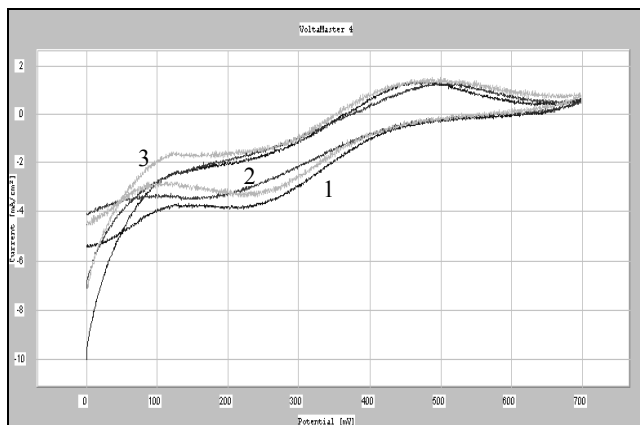


Figure 4. Platinum electrode,  $T = 40\text{ }^{\circ}\text{C}$ ; 5% KOH sol.,  $\text{K}_2\text{MnO}_4$  concentration is  $6 \cdot 10^{-2}\text{ M}$ ; Q concentration: 1 – 0; 2 –  $1.18 \cdot 10^{-2}\text{ M}$ ; 3 –  $1.18 \cdot 10^{-2}\text{ M}$ .

The introduction of Q into the system has approximately the same effect as at 25 °C – that is an increase of peak currents (similarly with introduction of  $\text{Mn}^{6+}$ ).

Obtained results in 10% KOH solution at 25 °C, by increasing  $\text{Mn}^{6+}$  concentration is presented in Fig. 5.

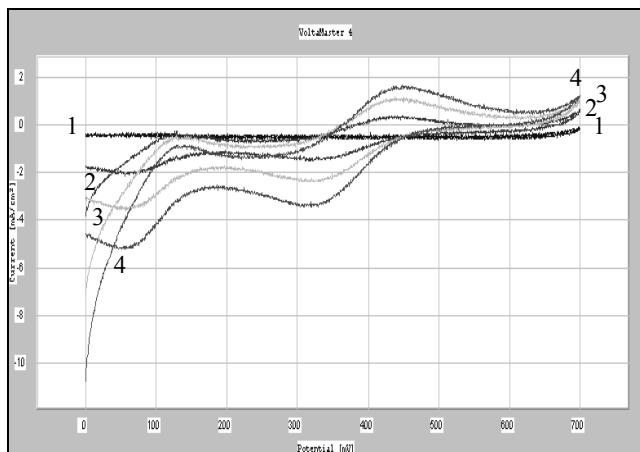


Figure 5. Platinum electrode,  $T = 25\text{ }^{\circ}\text{C}$ ; 10% KOH sol.,  $\text{K}_2\text{MnO}_4$  concentration: 1 – 0; 2 –  $2 \cdot 10^{-2}\text{ M}$ ; 3 –  $3.8 \cdot 10^{-2}\text{ M}$ ; 4 –  $6 \cdot 10^{-2}\text{ M}$ .

The major difference relative to the curves from figure 1 is the clear presence of the  $\text{Mn}^{3+}$  oxidation peak – at 120 mV – peak just suspected when we used 5% NaOH.

The introduction of quinoxaline into the electrolyte leads to the results from Fig. 6. The increase of Q

concentration has no major effects over the traced curves. The anodic peak from 440 mV increases very slightly, while the associated cathodic peak diminishes also very slightly. The same observations are valid for pair of peaks around the 100 mV value. In these conditions seems that the processes associated to these peaks are indeed reversible. Similarly in this case the cathodic peak diminishes his intensity by increasing the Q concentration while the anodic peak has slightly tendencies to increase. Anyway the differences between curves are not very pronounced but however the tendency seems to be the one we say.

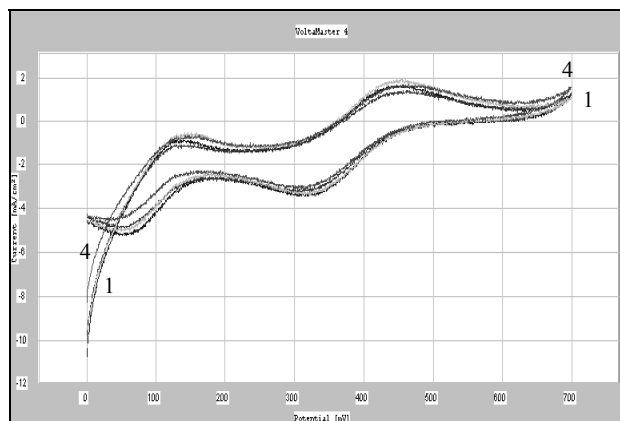


Figure 6. Platinum electrode,  $T = 25\text{ }^{\circ}\text{C}$ ; 10% KOH sol.,  $\text{K}_2\text{MnO}_4$  concentration is  $6 \cdot 10^{-2}\text{ M}$ ; Q concentration: 1 – 0; 2 –  $1.18 \cdot 10^{-2}\text{ M}$ ; 3 –  $2.04 \cdot 10^{-2}\text{ M}$ ; 4 –  $2.61 \cdot 10^{-2}\text{ M}$ .

The increase of temperature to 40 °C into 10 % KOH, in the presence of quinoxaline leads to curves from Fig. 7.

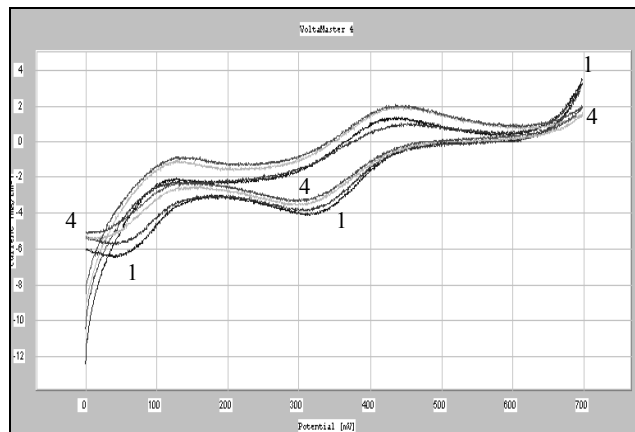


Figure 7. Platinum electrode,  $T = 40\text{ }^{\circ}\text{C}$ ; 10% KOH sol.,  $\text{K}_2\text{MnO}_4$  concentration is  $6 \cdot 10^{-2}\text{ M}$ ; Q concentration: 1 – 0; 2 –  $1.18 \cdot 10^{-2}\text{ M}$ ; 3 –  $2.04 \cdot 10^{-2}\text{ M}$ ; 4 –  $2.61 \cdot 10^{-2}\text{ M}$ .

Emerge from the figure that the anodic peaks increase in intensity and the cathodics diminish. The presence of quinoxaline in increasingly concentration, at 40 °C into 10 % KOH, leads to pronounced anodic processes –  $\text{Mn}^{6+}$  and  $\text{Mn}^{3+}$  oxidation – to their facilitation by increasing the concentration of the reactant species due to chemical reaction between Q and  $\text{KMnO}_4$  – that's why the peaks of the anodic currents increase. The same chemical reaction is responsible for consumption of the  $\text{Mn}^{7+}$  respectively  $\text{Mn}^{4+}$

and thereby for the diminishing of the cathodic peaks intensity. If the above mentioned equilibria shift to the formation of oxidized species, the processes becoming more irreversible.

Moreover the oxygen liberation shift to more positive potentials by increase of Q concentration – the phenomenon is clearly revealed by Fig. 9 – even if the scope of this study was not the investigation of this process. The effect is positive because has the effect to increase the utilization efficiency of the current in the desirable process –  $Mn^{7+}$  regeneration.

The effect of increasing the concentration of the main electrolyte – KOH from 5% to 10% – in the presence of Q is presenting in Fig. 8 and Fig. 9, at 25 respectively 40 °C.

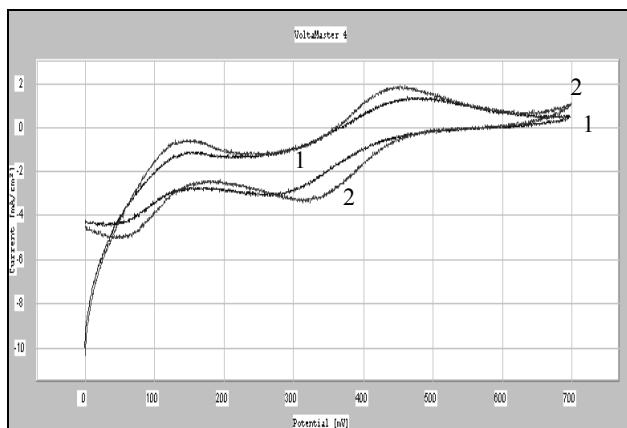


Figure 8. Platinum electrode; T = 25 °C;  $K_2MnO_4$  concentration is  $6.6 \cdot 10^{-2}$  M; Q concentration is  $2.04 \cdot 10^{-2}$  M; KOH: 1 – 5%, 2 – 10%.

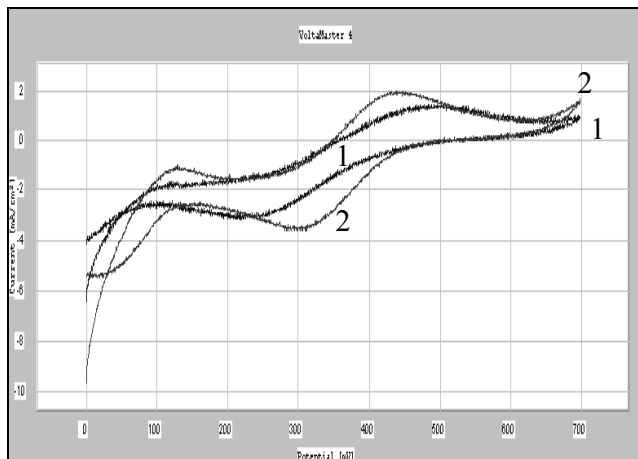


Figure 9. Platinum electrode; T = 40 °C;  $K_2MnO_4$  concentration is  $6.6 \cdot 10^{-2}$  M; Q concentration is  $2.04 \cdot 10^{-2}$  M; KOH: 1 – 5%, 2 – 10%.

Irrespective to temperature, increase of the main electrolyte concentration brings to the increase of the observed peaks and these shifts to more negative values – the anodic ones – and to more positive values – the cathodic ones. Hereby the potentials of the reversible processes (1) and (2) become more proximate. Should to mention the peaks evolution of the  $Mn^{4+}/Mn^{3+}$  at 40 °C, peaks which into 10 % KOH are strong defined while into 5 % KOH practically it missing.

The increase of main electrolyte concentration has a favorable effect over the electrode processes. Because

during the Q oxidation reaction is formed pyrazine-2,3-dicarboxylic acid, which reacts with KOH from electrolyte (forming its potassium salt) and consumes it, the keeping of a favorable conditions for development of the electrode reaction at optimum conditions is conditioned by careful control of the KOH concentration into electrolyte.

The increase of the temperature at constant concentration of KOH has the effect presented in Fig. 10 and Fig. 11.

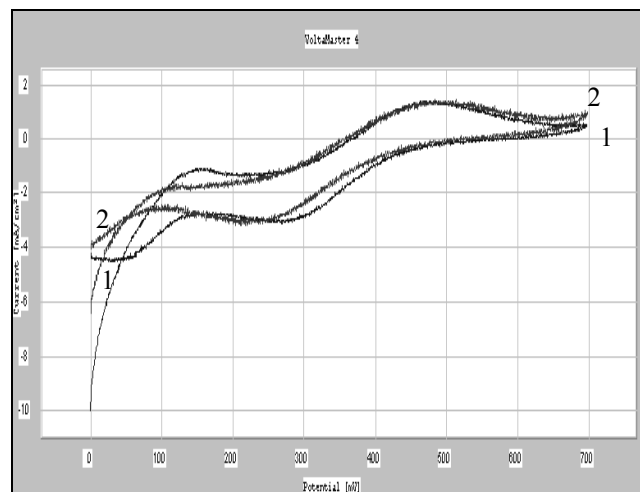


Figure 10. Platinum electrode;  $K_2MnO_4$  concentration is  $6.6 \cdot 10^{-2}$  M; Q concentration is  $2.04 \cdot 10^{-2}$  M; KOH sol.: 5%; T: 1 – 25 °C, 2 – 40 °C.

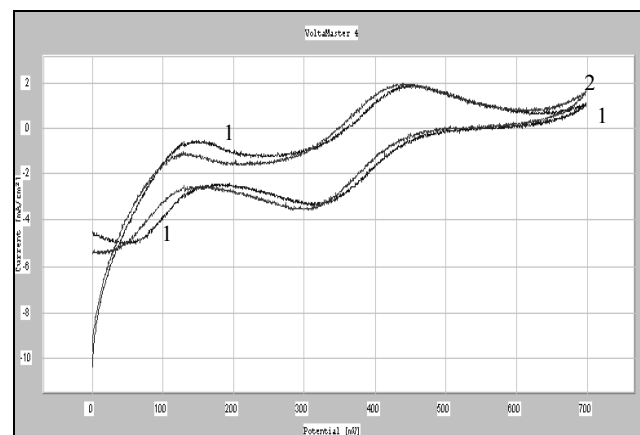


Figure 11. Platinum electrode;  $K_2MnO_4$  concentration is  $6.6 \cdot 10^{-2}$  M; Q concentration is  $2.04 \cdot 10^{-2}$  M; KOH sol.: 10%; T: 1 – 25 °C, 2 – 40 °C.

The effect due to temperature increase into 5% KOH is dignified in special at  $Mn^{4+}/Mn^{3+}$  couple – the curves which characterize this equilibrium practically disappear. Is observed a slightly shift of the  $Mn^{7+}$  reduction peak through more negative potentials.

The same effect at temperature increase is observed into 10% KOH – slightly modifications of the  $Mn^{7+}/Mn^{6+}$  couple peaks through more negative values – and the significant reduction of the intensity of the  $Mn^{4+}/Mn^{3+}$  equilibrium peaks. The increase of the temperature from 25 at 40 °C could have a favorable effect over  $Mn^{7+}$  regeneration through reduction of the current losses at

Mn<sup>4+</sup>/Mn<sup>3+</sup> couple and in this way a more efficient

#### 4. Conclusions

The investigation of the quinoxaline behavior on nickel electrode, into KOH solution containing potassium manganate has led at following conclusions:

- accordingly, in cyclic voltammetry studies effectuated on platinum electrode are observed two reversible processes associated to the Mn<sup>7+</sup>/Mn<sup>6+</sup> and Mn<sup>4+</sup>/Mn<sup>3+</sup> equilibriums;

- the increase of the K<sub>2</sub>MnO<sub>4</sub> concentration into the electrolyte bring to the increase of the anodic peaks and to the diminish of the cathodic ones – the quinoxaline presence has an effect similar to the increase of the Mn<sup>6+</sup> concentration;

- the increase of the KOH concentration leads to the increase of the intensity of the observed peaks;

- the increase of the electrolyte temperature leads to the diminished intensity of the peaks associated to the Mn<sup>4+</sup>/Mn<sup>3+</sup> process.

utilization of the current for Mn<sup>7+</sup> regeneration.

In conclusion, if we work on platinum electrode the increase of KOH concentration, the increase of temperature, of the Mn<sup>6+</sup> concentration and of quinoxaline favors the anodic regeneration process of the Mn<sup>7+</sup>. Furthermore, the presence of Q into electrolyte produces a significant reduction of the Mn<sup>3+</sup>/Mn<sup>4+</sup> couple weight, having a positive effect by increasing the process selectivity, reducing the weight and probability of MnO<sub>2</sub> forming and creating the premises for advantageous regeneration of the Mn<sup>7+</sup> with the purpose to use it in the chemical oxidation process of the quinoxaline to pyrazine-2,3-dicarboxylic acid.

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