ISSN: 2634 - 8853

Journal of Engineering and Applied Sciences Technology

SCIENTIFIC Research and Community

Review Article

Open Access

Formation of Organic Nitrates Mechanism of the Process

Bayramov RK

LLC "Olympia", Transportnaya Street 26, 301650 Novomoskovsk, Tula region, Russia

ABSTRACT

The analysis of the literature, including our works, was carried out, on the basis of which this review article was prepared. Previously, the direct (radiochemical) method proved the participation of nitrate ion in the anodic process - the oxygen evolution reaction (OER). Of interest was the possibility of accepting NO3 radicals formed during electrolysis by other anion-radical particles. Salts of acetic and propionic acids were chosen as model objects. It was found that during electrolysis of acetate-nitrate (system 1) and propionate-nitrate (system 11) mixtures, the pH of the medium significantly affects the selectivity of the reactions. In an acidic medium during electrolysis of both systems at high potentials, nitrate ion acts as a source of active oxygen, which is used to form molecular oxygen and destructively oxidizes alkyl groups. In a weakly alkaline solution, during the electrolysis of an equimolar mixture of system 1, ethane is formed, the current output (CO) of which drops sharply and reaches a value of ~30%, and a small amount of oxygen. A significant part of the current is spent on the oxidation of CH3 particles with the formation of carbon dioxide (CO ~60%) and water. In a weakly alkaline solution, the process of system 11 differs from system 1 and is interesting in that during the electrolysis of an equimolar mixture of propionate and nitrate, products of the interaction of nitrate radicals and propionate particles are formed with the formation of organic nitrates. Based on the analysis of the data obtained by a set of methods, a mechanism for the formation of organic nitrates is proposed.

***Corresponding author**

Bayramov RK, LLC "Olympia", Transportnaya Street 26, 301650 Novomoskovsk, Tula region, Russia.

Received: August 21, 2025; **Accepted:** September 05, 2025; **Published:** September 26, 2025

Keywords: Electrolysis, Anion, Potential, Oxidation, Electrolyzer, Membrane

Introduction

The interest of researchers in electrode processes occurring at high anodic potentials is due to the possibility of selective synthesis of valuable products. The occurrence of various reactions at the anode, their high sensitivity to mutual influence, as well as strong dependence on external conditions make the production of final products one of the most complex processes. From the experimental materials described in the literature, it is difficult to draw an unambiguous conclusion about the presence of a deep connection between these reactions and the influence of the state of the electrode surface on the kinetics and mechanism of the process. In, the participation of nitrate ion in the anodic process, the oxygen evolution reaction (OER), was proven by a direct (radiochemical) method [1]. In this paper, based on indirect data, a mechanism for the oxidation of nitrate ions was proposed that assumes the occurrence, along with the main mechanism, of a second mechanism, when unstable nitrate radicals (NO3) formed during electrolysis dimerize to form an unstable dimeric product, nitrogen peroxide (N2O6), with its subsequent decomposition into nitrogen dioxide and oxygen. Of interest was the possibility of accepting NO3 radicals obtained during electrolysis by other anion-radical particles. Acetic and propionic acid salts were chosen as the model. This was due to the fact that the process of acetate ion oxidation has been studied in detail and covered in the literature [2-11]. In addition, the fact of formation of organic nitrates during electrolysis of the propionate-nitrate mixture is known.

Features of The Anodic Behavior of The Propionate Ion at High Anodic Potentials

Unlike acetic acid ions, the kinetics, mechanism, and state of the anodic surface during the electrolysis of propionates have been studied much less [12-16]. During the electrolysis of propionates, instead of the expected products of the Kolbe synthesis (butane and carbon dioxide), ethylene is formed in the process with a current efficiency of (CO ~ 60%) and small amounts of butane (CO ~ 10%), ethane (CO ~ 5%), ethyl acetate, ethanol, and ethyl propionate. Since ethylene plays an important role in obtaining organic nitrates during the electrolysis of a mixture of nitrate and propionate, much attention has been paid to its formation. The authors having subjected solutions of propionates in which α- and β-carbon atoms were labeled to electrolysis, found that the formation of ethylene is accompanied by the splitting off of the β-carbon atom [12,13]. The mechanism of the process, which is reduced to the reaction of disproportionation of alkyl radicals:

$$2C2H5 - -2e \rightarrow 2C2H5^* + CO2 \quad (1)$$

$$2C2H5^* \rightarrow C2H4 + C2H6, \quad (2)$$

is not fully substantiated, since the current output (CO) of ethane is small (~5%), while, according to this mechanism, its high yield, equal to the CO of ethylene, should be expected. In the work, where the process of propionate oxidation was also studied, the formation of ethylene occurs according to the following scheme [14]:

$$C2H5^* + C2H5COO^* \rightarrow C2H4 + C2H5COOH \quad (3)$$

In our opinion, this mechanism is not fully proven, since it assumes surface recombination of radical particles C2H5* and C2H5COO* with simultaneous splitting off of a proton in C2H5*. It is known that carboxylate radicals are very unstable and it is difficult to retain them on the electrode surface in a sufficient concentration necessary for this reaction to occur. As for the mechanism, which is reduced to the surface recombination of particles C2H5COO* and OH* with subsequent decomposition of the intermediate complex [15]:

$$C2H5COO^* + OH^* \rightarrow C2H4 + CO2 + H2O \quad (4),$$

it is also not entirely justified due to the above reasons.

A combination of methods (electrolysis at a controlled potential, impedance measurements, a radiochemical method) was used to study the anodic oxidation of propionate in an aqueous solution [16]. It was shown that during electrolysis in the region of anion discharge, ethylene (CO ~ 62%), butane (CO ~ 10%) and small amounts of carbon dioxide, ethanol, ethylpropionate and acetal aldehyde are formed. The proportion of carbon dioxide obtained during the destructive oxidation of alkyl particles was determined using the labeled atom method. The influence of the potential, solution concentration and electrolysis temperature on the current efficiency of the electrolysis products was studied. Based on the analysis of the data obtained using a set of methods, the authors proposed a mechanism for the formation of ethylene, which is reduced to the deprotonation of radical particles C2H5:

$$C_2H_5^* - e \rightarrow C_2H_4 + H^+ \quad (5).$$

This mechanism does not contradict the experimental data obtained.

Formation of Organic Nitrates

Organic nitrates were first obtained electrochemically by electrolysis of a mixture of nitric and monocarboxylic acid salts and described in [17-20]. The authors studied in detail the electrolysis conditions (electrolyte concentration, pH of the medium, electrolysis temperature, nature of carboxylic acid salts, etc.) on the efficiency of organic nitrate formation. They found a direct relationship between the amount of unsaturated hydrocarbons and the current efficiency of organic nitrate formation. The mechanism of organic nitrate formation was not studied in detail, and the following process scheme was proposed:

$$CnH2n + HNO3 \rightarrow C2H2n+1NO3 \quad (6)$$

$$2CnH2n + 2HNO3 + O \rightarrow CnH2n(NO3)2 + H2O \quad (7)$$

Organic nitrates were also obtained by electrolysis of nitrates in the presence of ethylene in water-acetone solutions. It was suggested that the primary process is the discharge of the nitrate ion and the subsequent interaction of the formed particle with ethylene according to the reaction:

$$CH2 = CH2 + 2NO3ads. \rightarrow ONOCH2CH2ONO2 \quad (8)$$

The proposed reaction is also unlikely due to the instability of the NO3 radical, and this mechanism cannot be considered justified without proof of ethylene adsorption on the electrode.

The mechanism of synthesis of organic nitrates has been studied in most detail in non-aqueous solvents. Its main feature is the formation of an intermediate carbocation and the NO3 radical. The mechanism of these reactions differs fundamentally from the mechanism of the process in aqueous media, in which the formation of organic nitrates is associated, as shown above, with the appearance of compounds with multiple bonds in the reaction zone.

In connection with the increased use of organic nitrates in various fields of technology, we will also consider some other ways of their synthesis. In, homogeneous catalytic oxidation of olefins into glycol nitrates in the presence of a Pd (11) complex was studied [21,22]. The mechanism of this interesting process is reduced to the formation of Ϭ -palladium-organic complexes with their subsequent decomposition to glycol nitrates, which are further oxidized by nitric acid to the corresponding nitrates. There are also other chemical routes to the synthesis of organic nitrates, for example, nitration of alcohols with a sulfur-nitrogen mixture [23]. However, in a number of cases, chemical routes do not always give the desired results for obtaining specific inorganic and organic nitrates, and the electrochemical method for their preparation can become decisive. Since the review paper analyzes the works available in the literature, we will present in some more detail the experimental results and their discussion obtained by us in studying the behavior of the nitrate ion during electrolysis in a binary mixture (nitrate-acetate and nitrate-propionate).

Experimental Part

During the research (study of electrolysis products, kinetics and mechanism of the process) the electrolyzers and devices previously described in were used [24]. The potential was measured against normal hydrogen or saturated calomel electrode. The potential values in salt solutions and in a mixture of nitric acid with sodium acetate or propionate are given in relation to a reversible hydrogen electrode in the same solution (φr.). The amount of electricity passed through was recorded using a coulometer.

Electrolyte solutions were prepared on bidistillate nitric acid of special purity, twice distilled acetic and propionic acids and twice recrystallized their salts.

To determine the balance of electrolysis products, the released anode gases (O2, CO2, C2H4 and C4H10) were first passed through a trap with a neutral buffer solution of potassium iodide to separate and quantify ozone and then collected in a calibrated gas burette. Gas samples were taken from the latter and analyzed chromatographically using a thermal conductivity detector on a Tsvet-1 chromatograph. Calibration was carried out using standards such as oxygen, carbon dioxide, ethylene, butane, and ethane. Before calculating the current output (CO) of the products, the gas volumes were brought to normal conditions. During electrolysis of the propionate-nitrate mixture, a mixture of products is formed as a separate liquid phase: ethyl nitrate (EN), butyl nitrate (BN), ethyl propionate (EP), 1,2 ethylene glycol dinitrate (1,2 EGDN) and 1,4 butylene glycol dinitrate (1,4 BHDN). Since these substances interact with metal surfaces, glass columns were used with the analyzed sample introduced directly into the column. The analysis of the products was carried out on a Tsvet-100 chromatograph using two detectors: thermal conductivity and ionization-flame. In the first case, the column temperature was + 250C, in the second - + 1500C. Chromaton N-AW-DMCS impregnated with 5% silicone SE-30 was used as an adsorbent. To study the mechanism of the oxidation process of the propionate ion in pure propionate or in a mixture of propionate with nitrate, it is important to know the proportion of CO2 formed

during the oxidation of the alkyl group.

Modern radiochemical methods are reduced either to determining the change in the concentration of the labeled adsorbate in the solution, or to determining the activity of the substance on the electrode in the solution or after washing it under specified conditions (the "electrode" method). An exhaustive description and critical analysis of them is given in [25].

The only method that allows studying adsorption at high potentials from concentrated solutions is the "electrode" method. This method, as applied to high potentials, was developed in [26-28]. A significant drawback of the method is the need to interrupt polarization and conduct measurements after washing the electrode. Nevertheless, the results obtained by different authors are in fairly good agreement with each other, and this gives grounds to consider this method sufficiently reliable for studying adsorption at high potentials [6,26-28]. The activity of the electrodes was measured using the setup shown in Figure 1.

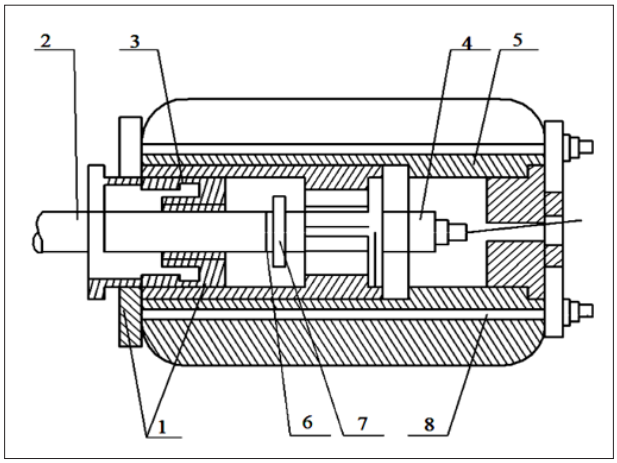

Figure 1: Electrode Activity Determination Device

1 - System for Fine Adjustment of the Distance Between the Electrode and the End-Type Counter; 2 - Glass Electrode Body; 3 – Ground Joint for Electrode Attachment; 4 - Radioactivity Counter SBT-7; 5 - Lead Case; 6 - Platinum Electrode; 7 – End-Type Counter Window; 8- Tie-Down Bolts.

The activity of the electrodes was measured using a Geiger counter SBT-7 and a device that allowed the distance between the electrode and the counter to be adjusted (1). The pulse recorder was a PP-16 device with a BGS-4 preamplifier. The isotope C14, contained in the ethyl group, was used as an indicator in the study of propionate adsorption. To calibrate the counter, 0.1 ml of a standard solution of known concentration (~1014 ÷1015 atoms), obtained by diluting the working solution, was applied to the substrate and dried under an electric lamp, then its activity was measured. The studies were carried out in a cell with a cooled platinum anode with a visible surface of ~4 cm2 (see Figure 4) [24]. The working volume of the anode space was 25 ml. The carbon dioxide (CO2) released during electrolysis was quantitatively absorbed in a 30% NaOH solution and analyzed using the SBS-1 setup. The specific activity of the solution was measured in glass weighing bottles, into which 5 ml of the analyzed alkaline solution and 0.2 g of scintillation granules (average diameter 50 μm) were introduced. The fraction of CO2 (Pi) formed during oxidation of the alkyl group was calculated using the formula:

$$Pi=22,4\cdot C_0\frac{NV1}{NoVo} \quad (1)$$

where Co is the concentration of sodium propionate in the reference solution (mol/l), N is the relative specific β-activity of the solution containing absorbed carbon dioxide (imp/min), N0 is the relative specific β-activity of the reference solution (imp/min), V0 is the volume of absorbed CO_2 in the alkaline NaOH solution (ml), V1 is the volume of the alkaline solution (ml). Pi – in our experiments was determined with a relative root mean square error of ± 10% from the arithmetic mean of 5÷ 6 measurements

Sodium propionate labeled in the ethyl or carboxylate groups with the isotope C14 was introduced into the studied system (propionate solution or a mixture of nitrate and propionate). The specific activity of the working solution was 2•10-2 mCi/ml. The reference solution was prepared from the working solution by diluting it 250 times with 30% NaOH solution. The experimental procedure was previously developed and standardized to ensure reproducible results. The electrode under study was polished with fine grinding powder, treated for 5 minutes in a mixture of hydrogen peroxide and sulfuric acid (in a ratio of 3:1), and 2 minutes in bidistillate water (600C). To completely remove the activity, the electrode was additionally cathodically polarized at a potential of – 1 V for 3 minutes in 1N sulfuric acid. Then, cathode-anodic activation was carried out in a nitrogen atmosphere until potentiodynamic curves of hydrogen deposition were obtained, according to which the true electrode surface was estimated in each experiment. Then, after measuring the background, the electrode was transferred to a cell with an active solution and polarized at a given potential for 5 minutes. During this time, as was established in preliminary experiments, stationary adsorption was achieved. The electrode washing mode plays an important role in adsorption measurements. Depending on the washing time, different amounts of adsorbed particles on the electrode can be measured, so in our measurements the washing time was strictly controlled, and the washing mode was standardized. When studying "stationary" adsorption, the electrode was immediately washed in bidistillate water for 5 or 8 minutes, depending on the nature of the activity decay curve over time. To assess "weakly bound" particles on the electrode, washings were carried out for short periods of time - 1.3 and 10 seconds, after which the glass part of the electrode was wiped with alcohol of the extra pure brand "EPB", then the electrode surface was dried before measurement then the electrode surface was dried before measurement. The electrode wash curve was found to be described by two exponents and indicated the presence of at least two forms of adsorption - less strong (first seconds of wash) and stronger (minutes). The reproducibility of adsorption values on the same electrode was 5÷10%.

Results and Discussion

To determine the possibility of accepting adsorbed unstable radical NO3 particles in the electrochemical synthesis reaction, the nature of their interaction with the products of the discharge of some carboxylic acid anions was traced Acetate and propionate ions were chosen as model ions.

Figure 2 shows the polarization curves and the corresponding changes in the capacity of the double electric layer from the potential for acetate-nitric acid and propionate-nitric acid mixtures, as well as the changes in the capacity with potential for a nitric acid solution.

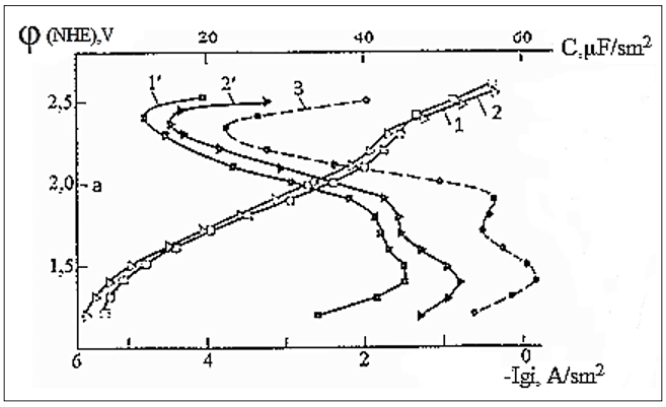

Figure 2: Polarization Curves (1,2) and Capacity Dependence (1′,2′,3) on Pt Electrode in Solutions

1, 1′ – 0.5N C2H5COONa + 0.5N HNO3;
2, 2′ – 0.5N CH3COONa + 0.5N HNO3;
3 – 1N HNO3

It is evident from the figure that in acidic solutions the character of the change in capacity with potential in the region of anion discharge for mixtures (curves 1′ and 2′) is the same as for pure nitric acid (curve 3). The properties of the anode surface under these conditions are determined by the inorganic component and it can be assumed that the adsorption of acetate and propionate particles is small.

On the contrary, in weakly alkaline media (Figure 3). the course of the C - φ curves for mixtures (curves 1′ and 2′) is close to the character of the change in capacity with potential for pure acetate and propionate solutions (curve 4) and differs greatly from that for the sodium nitrate solution. (curve 3).

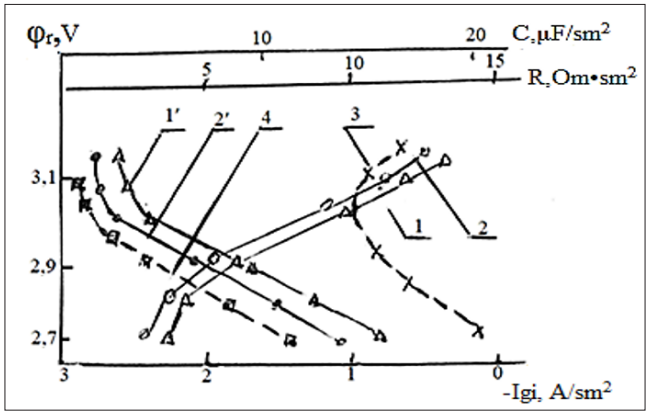

Figure 3: Polarization curves (1, 2) and capacity dependence (1′, 2′, 3, 4) on Pt electrode potential for alkaline solutions
1, 1′ – 0.5N C2H5COONa + 0.5N NaNO3;
2, 2′ – 0.5N CH3COONa + 0.5N NaNO3;
3 - 1N NaNO3; 4 - 1N C2H5COONa (1N CH3COONa)

It should be assumed that in this case the state of the electrode surface is determined by the adsorption of organic particles, which is confirmed by the data on the adsorption of propionates in the presence of NO3-- ions, obtained using labeled carbon.

Thus, in acidic environments at high potentials, even at high concentrations of introduced acetate and propionate ions (up to 3N), the main share of the current (85-90%) is spent on the oxidation of the NO3-- ion with the formation of active oxygen. The resulting active oxygen is spent mainly on the release of molecular oxygen, and only an insignificant part of it (~10÷15%) goes to the destructive oxidation of alkyl groups.

In alkaline media in the presence of cations at high potentials, simultaneous discharge of organic and inorganic anions occurs. In the acetate-nitrate system, no products of mutual acceptance of the components being discharged are observed (ethane, carbon dioxide, and oxygen are formed), while in the propionate-nitrate mixture, some of the NO3- ions being discharged interact with the products of propionate ion discharge to form organic nitrates [29]. The observed difference in the nature of the products being formed in these two systems is due to the difference in the properties and behavior of organic radicals primarily generated on the electrode surface. This conclusion is consistent with the data on the study of electrolysis products in these systems. A study of the electrolysis products of acetate-nitrate (system I) and propionate-nitrate (system II) mixtures on a platinum anode showed a strong dependence of the selectivity of the reactions on the pH of the medium. In acidic environments, during electrolysis of acetate-nitrate and propionate-nitrate mixtures in a wide temperature range (+200C ÷ -200C) at high potentials (above 2.2V), the main product is oxygen, obtained during the discharge of NO3- ion and water. In this case, carbon dioxide is formed in small quantities. For example, at a potential of 2.6 V, the oxygen and CO2 contents are 85% and 14%, respectively, in the acetate-nitric acid mixture and 71% and 26%, respectively, in the propionate-nitric acid mixture. At φr = 2.6 V, using labeled carbon in alkyl groups, the proportion of CO2 (Pi) formed during the destructive oxidation of alkyl particles was determined according to the reaction:

$$CH3\ ads. + 3.50ads. \rightarrow CO2 + 1.5H2O \quad (9),$$

$$C2H5\ ads. + 6.5\ 0ads. \rightarrow 2CO2 + 2.5H2O \quad (10),$$

The proportion of CO2 (Pi) was 45 ± 5% for I and 64 ± 5% for II systems. The data obtained suggest that the discharged organic ions in both cases are completely subject to destructive oxidation.

The data on the destructive oxidation of alkyl particles in weakly alkaline solutions, as well as in acidic media, were determined using labeled carbon. Table 1 presents the results of balance experiments for equimolar mixtures of acetate-nitrate (I) and propionate-nitrate (II) at pH ~ 11, φ = 3.14V, t = + 20^{0}C.

Table 1: Current Output of Electrolysis Products 1 and 11 Systems

System	Organic nitrate	C_2H_6	C_2H_4	CO_2*	O_2
3N CH_3COONa +3N $NaNO_3$ (I)	-	33.6	-	60	5.0
3N C_2H_5COONa +3N $NaNO_3$ (II)	40.5	-	3.5	50	4.5

The table shows that in system I, as in pure acetates, ethane is formed, but its CO is reduced to 33% and a small amount of oxygen (CO= ~5%). A significant part of the current, compared to the pure system, is spent on the destructive oxidation of CH3 radicals to water and CO2. (the current output of CO2 in the mixture is 60% versus 15% in pure acetates). The fraction of current spent on oxidation of the organic (CH3COO-) component calculated from these data for a potential of 3.1 V is 40%, and for the inorganic (NO3- ion, water) it is about 60%. The process in system II differs from system I and is interesting in that in this

case products of mutual acceptance of the discharging components are formed - a mixture of organic nitrates, which are released as a separate liquid phase [28]. Chromatographic analysis of the mixture showed that it contains ethyl nitrate (EN), butyl nitrate (BN), 1,2 ethylene glycol dinitrate (1,2 EGDN), 1,4 butylene glycol dinitrate (1,4 BHDN) and ethyl propionate (EP). In the gas phase, ethylene, butane, CO2 and oxygen are formed. The fraction of current spent in this case on discharging the organic component is ~34%. The remaining 66% of the current goes to discharge the NO3 ion and water. However, unlike system I, where the discharged NO3 ions go to form oxygen and destructive oxidation of CH3 radicals, in system II a part of the discharged NO3 ions is consumed in the process of formation of organic nitrates.

Since organic nitrates are formed during the electrolysis of weakly alkaline solutions of a mixture of salts of propionic and nitric acids, the main attention was paid to the study of the processes occurring in this system.

For a complete calculation of the CO of the electrolysis products in this system, the proportion of CO2 (Pi) formed during the destructive oxidation of C2H5 particles was determined using the labeled atom method. The dependence of Pi on the electrode potential and the concentration of nitrate ion is shown in Figure 4 a, b.

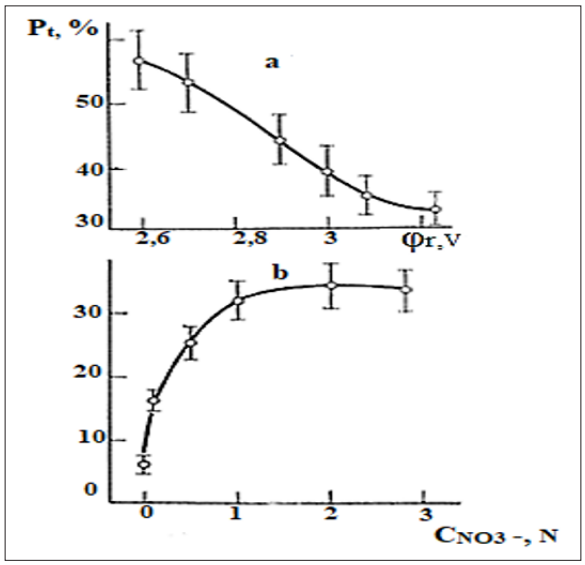

Figure 4: Change in the share of CO2 (Pi) formed from the ethyl group in solutions of propionate and sodium nitrate mixture depending on:
a: Potentials (3N C2H5COONa + 3N NaNO3),
b: Concentrations of the Nitrate Ion (3N C2H5COONa + xN NaNO3), at φr= 3.1V.

The general course of the Pi – φr curve in this system remains the same as in a pure propionate solution. With an increase in potential from 2.6 to 3.0V, Pi decreases sharply from 57% to 38% and then changes insignificantly to 32%. However, in absolute values, Pi in this system is several times greater than in pure propionates (32 versus 4%). The latter is obviously associated with a large amount of active oxygen in the presence of a discharging NO3- ion, which is clearly confirmed by the data on the change in Pi with the concentration of the nitrate ion (Figure 4 b).

As noted above, during the electrolysis of the propionate-nitrate mixture at high potentials in the gas phase, the following are formed: ethylene, carbon dioxide, butane, oxygen, and in the liquid phase: ethyl nitrate; butyl nitrate; 1,2-ethylene glycol dinitrate; 1,4 butylene glycol dinitrate and ethyl propionate.

Figure 5 shows the current output (CO) distribution of the main electrolysis products of an equimolar mixture of propionate and sodium nitrate from the electrode potential.

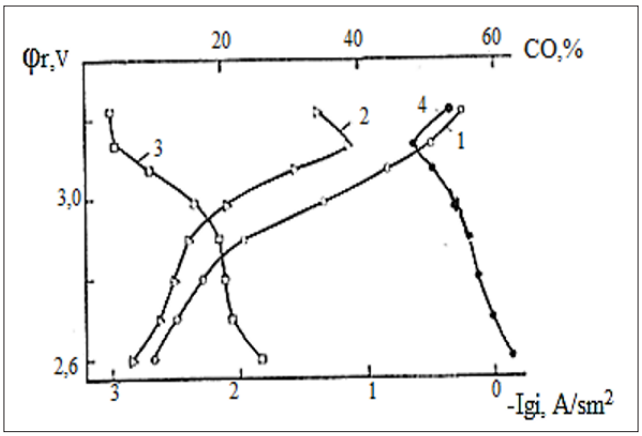

Figure 5: Dependence of the CO of the electrolysis products on the potential of the Pt electrode and the general polarization curve (1) in solution – 3N NaNO3 + 3N C2H5COONa, pH ~11, t = + 20 °C; 1 - Polarization Curve; 2 - Organic Nitrates; 3 - Oxygen; 4 - CO2 Formed from the Alkyl Group.

It is evident that the total CO of organic nitrates increases slowly at first ~ up to 10% at φr = 2.9 V, and then more sharply, reaching 40% and then falling slightly. The CO of oxygen changes antibatically with the potential, the CO of carbon dioxide formed during the destructive oxidation of C2H5 radicals changes practically little with the potential, remaining within 50 ÷ 60%. The dependence of the BT of individual organic nitrates on the potential is shown in Figure 6.

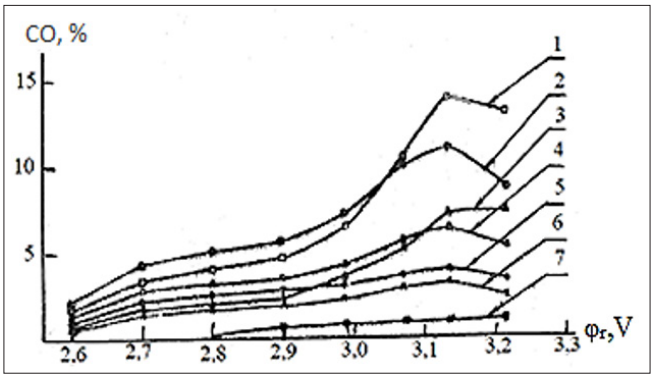

Figure 6: Dependence of the CO of the electrolysis products on the Pt electrode potential in the solution: 3N NaNO3 + 3N C2H5COONa, pH ~ 11, t = + 20 °C.

1- 1,4-Butylene Glycol Dinitrate, 2 - 1,2-Ethyleneglycoldinitrate, 3 - Butylnitrate, 4 - Ethylnitrate, 5 - Ethylene, 6 - Ethylpropionate, 7 - Butane.

It follows from the figure that the nature of the change in the current output (CO) of 1,4 butylene glycol dinitrate (curve 1), 1,2 ethylene glycol dinitrate (curve 2), butyl nitrate (curve 3), ethyl nitrate (curve 4) remains the same as for their sum, and nitrates with two NO3 groups are formed with the highest current output-

1,4 BHDN and 1,2 EGDN (14% and 11%). The dependence of the current output of ethylene, ethyl propionate and butane is described by curves 5, 6 and 7. CO of ethylene changes little with potential, remaining within 2-3%, which is much less than in pure propionates, where the current yield of C2H4 = ~60%. This is due to the fact that C2H5 radicals consumed in the process of ethylene release through the intermediate formation of the ethylene complex in pure propionate, in the presence of discharged NO3- - ions, are practically quantitatively consumed in the process of formation of organic nitrates. The latter follows from the calculation of the CO of individual organic nitrates in comparison with the CO of ethylene in a pure system. This is also indicated by the data on the change in the current yield and the rates of formation of electrolysis products from the concentration of the NO3- - ion in the solution.

The dependence of the current yield of the electrolysis products on the concentration of nitrate ion (the concentration of propionate is constant and equal to 3N) is shown in Figure 7.

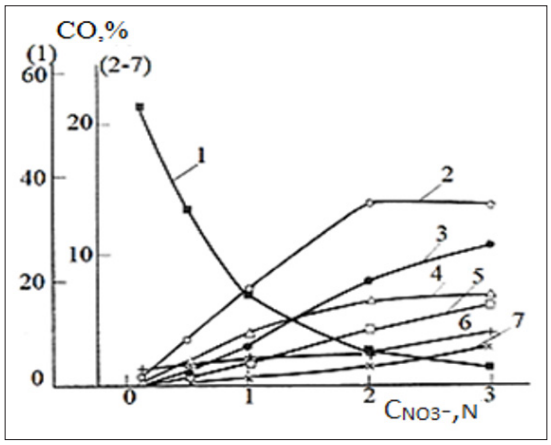

Figure 7: Dependence of the CO of the Electrolysis Products on the Concentration of Nitrate Ion (Propionate Concentration is Constant and Equal to 3N) for a Potential of 3.1 V at pH = ~ 11 and t = + 20 °C.
1 - Ethylene, 2 - 1,4-Butyleneglycoldinitrate, 3 - 1,2-Ethyleneglycoldinitrate, 4 - Butylnitrate, 5 - Ethylnitrate, 6 - Oxygen, 7 - Ethylpropionate.

Partial currents of formation of ethylene and organic nitrates as a function of nitrate ion concentration (propionate concentration remained constant and equal to 3N) for a potential of 3.1 V at pH = ~ 11 are shown in Figure 8.

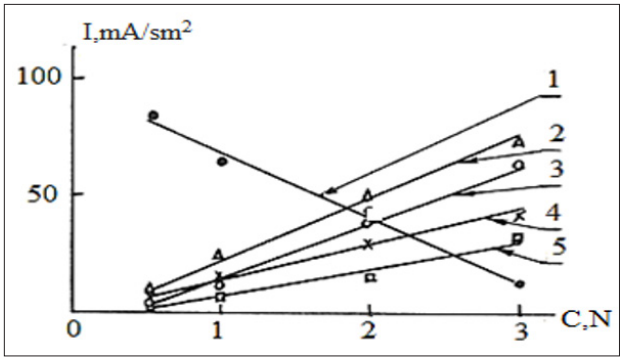

Figure 8: Partial Currents of Formation of Ethylene (1), 1,4-Butylene Glycol Dinitrate (2), 1,2-Ethylene Glycol Dinitrate (3), Butyl Nitrate (4) and Ethyl Nitrate (5) As a Function of Nitrate Ion Concentration (Propionate Concentration is Constant and is Equal to 3N) for Potential of 3.1 V at pH = ~ 11 and t = +20^0 C

The formal orders of reactions for nitrate ion for BN, EN, 1,4 BHDN, 1,2 EGDN calculated from these data are 1.1; 1.2; 1.3; 1.8, respectively. On the other hand, the mixture exhibits a low value of the butane CO compared to pure propionate, which remains virtually unchanged with the potential and concentration of the nitrate ion, as well as high values of the carbon dioxide CO formed during the destructive oxidation of C2H5 radicals. The calculation based on the data of the balance experiments and the Pi values showed that those C2H5 radicals that are spent on the formation of butane in pure propionates (CO ~ 15%) are subject to mainly destructive oxidation in the presence of discharging NO3- - ions. This agrees with the results on the excess of the current output CO2 formed during destructive oxidation in the mixture compared to pure propionate. Based on the data obtained, it is possible to estimate, as a first approximation, the shares of the current spent on the oxidation of individual components of the solution. This estimate was carried out as follows. Initially, the shares of current consumed during the oxidation of organic (I C2H5COO-) and total inorganic (I H2O and NO3-) components of the solution were determined. I C2H5COO -, which was calculated by summing up the shares of the current spent on the formation of ethylene, ethyl propionate, C2H5 radicals undergoing destructive oxidation and consumed in the process of formation of organic nitrates. The partial discharge current of the nitrate ion was determined by summing up the shares of the current spent on the formation of organic nitrates and active oxygen from the NO3 - ion consumed during destructive oxidation. For a mixture of 3N C2H5COONa + 3N NaNO3 at high potentials, it can be assumed that almost all the active oxygen consumed during destructive oxidation is taken from the discharging NO3 - ions. This follows from the fact that the maximum possible share of the current spent on discharging water in pure systems of the corresponding concentrations (5 ÷ 6N) is ~ 7 ÷ 10%. The data of such an assessment for a potential of 3.1 V in a mixture of 3N C2H5COONa + 3N NaNO3 are presented in Table 2.

Table 2: Fractions of the Current Going to the Oxidation of Individual Solution Components

İ tot., mA/sm²	İ NO_{3-}, mA/sm²		İ C_2H_5COO, mA/sm²				İ H_2O, mA/sm²
220 (100 %)	110 (50%)		75 (34%)				25 (10%)
	İ org. nitr.	İ destr. oxidation	İ C2H4	İ ethyl prop.	İ org. nitr.		
	37 (~17%)	77 (~35%)	6.6 (~ 3%)	9 (4~ %)	9 (~4%)	53 (~24%)	

The table shows that ~ 50% of the total current is spent on discharging the nitrate ion, ~ 37% on discharging the propionate ion, and ~ 10% on discharging the water. In this case, 1/3 of the discharged NO3- ions are spent on the formation of organic nitrates, and the remaining 2/3 are spent on the destructive oxidation of C2H5 radicals. When introducing small concentrations of nitrate ion into a propionate solution at high potentials, the discharged NO3- ions are consumed mainly in destructive oxidation, and only a small part is spent on the formation of organic nitrates Thus, in the mixture 3N C2H5COONa + 0.5N NaNO3 at φr = 3.1 V, the ethylene CO decreases from 60% (in pure propionates) to ~ 37%. The CO of organic nitrates in this mixture is 6%, and Pi increases from 6% to 27% compared to pure propionate. Under the same conditions, in the mixture 3N C2H5COONa + 1N NaNO3, the ethylene CO is ~ 20%, the CO of organic nitrates is 15%, and Pi is ~ 30%. It follows that with an increase in the surface concentration of NO3 radical particles, the probability of its acceptance with the formation of organic nitrates increases.

The data of the balance experiments correlate with the results of studying the state of the electrode surface. When adding a nitrate ion to a propionate solution, the capacity of the double electric layer changes almost insignificantly, remaining within 0.5 μF/cm2. In another case, when a propionate ion is added to a nitrate solution to a concentration of 0.5N, the capacity drops sharply from 20 μF/cm2 to 1 μF/cm2 and then remains practically unchanged with an increase in the concentration of C2H5COO- ions. Probably, the introduction of NO3- ions has little effect on the adsorption of the products of the discharge of propionate ions.

This conclusion is in good agreement with the data on the effect of NO3- ions on the adsorption of propionates obtained by the method of labeled atoms. The adsorption from a 1N propionate solution was determined in advance at a constant pH in the solution volume. Then, a calculated amount of sodium nitrate was added to this solution (initially small concentrations, for example, 0.05N) and the adsorption of propionate in this mixture was determined. The adsorption of propionate was determined in the same way when introducing other concentrations of nitrate ion. The results obtained for a potential of 3.0 V are given in Table 3.

Table 3: Adsorption of Sodium Propionate Depending on the Concentration of Nitrate Ion Added to the Solution

Additions of NO_3^-, (N)	G.10^{14} part. /sm²
0	2.54
0.055	2.37
0.109	2.23
0.500	2.27
1.00	2.26

As can be seen from the table, with the introduction of NO3- ions, the adsorption of propionates decreases insignificantly (by ~ 10%). Comparison of these data with the results of balance experiments gives grounds to assume that the electrode surface is filled mainly with relatively tightly bound products of the propionate ion discharge (of the order of a monolayer), and the concentration of ethylene complexes is low.

The set of data obtained allows us to conclude that the synthesis of organic nitrates occurs at a sufficient degree of filling of the NO3 surface with radical particles, through the intermediate formation of C2H4NO3ads., arising during the interaction of discharging NO3- ions with ethylene complexes at the moment of their formation:

C2H4 ads. + NO3 ads. → C2H4 NO3 ads. (11)

For this reaction to occur, the rate of accentuation of radical NO3 particles along multiple bonds must be higher than the rate of interaction of NO3 ads. with the release of oxygen. These findings are in good agreement with the data on the dependence of the CO of the electrolysis products on the temperature (Figure 9).

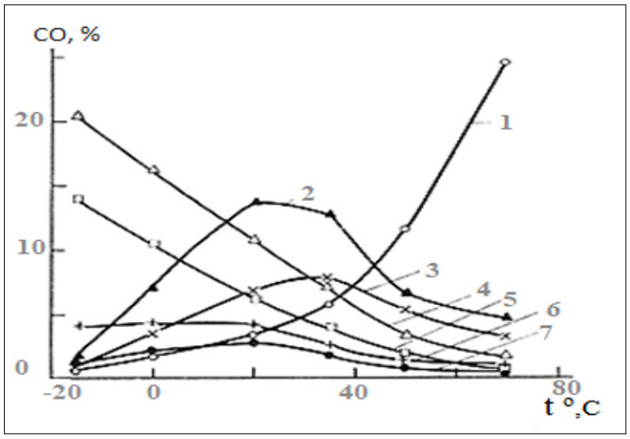

Figure 9: Temperature Dependence of CO Yields of Electrolysis Products. Solution 3N C2HCOONa + 3N NaNO3, ϕr = 3.1 V, pH = ~ 11
1 - Ethylene, 2 - 1,4-Butylene Glycol Dinitrate; 3 - Butyl Nitrate; 4 - 1,2-Ethylene Glycol Dinitrate; 5 - Ethyl Nitrate; 6 - Oxygen; 7 - Ethyl Propionate.

It follows from the figure that the current output (CO) of ethylene drops sharply with decreasing temperature. The current output of individual organic nitrates depends on temperature differently. With decreasing temperature, the CO of 1,2-EGDN and EN increases, and the current efficiency of BN and 1,4-BHDN pass through a maximum. It is interesting to note the different effect of temperature in two intervals: (interval 1 - +70 ÷ +200C) and (interval 11 - +20 ÷ -200C). With decreasing temperature in the

first interval, the CO of ethylene sharply drops from 25% to 1 ÷ 3% and the CO of all organic nitrates increases. As noted earlier, in the pure propionate system, the CO of ethylene is practically independent of temperature. At the same time, with decreasing temperature, the radical particles NO3 stabilize. This gives grounds to assume that in the first interval (+70 ÷ +200C), with decreasing temperature, the surface concentration of intermediate particles C2H4 NO3 increases. In this case, the rate of NO3 addition to the double bond at the moment of its formation is higher than the rate of detachment of the C2H4 particle with the formation of ethylene and the rate of decomposition of the radical particle NO3 with the formation of oxygen. In the second temperature range (+20 ÷ -200C), a change in the ratio of the rates of formation of organic nitrates is observed. This may indicate that in this temperature range the proportion of C2H5 radicals on the electrode surface that participated in the formation of ethylene is almost completely bound to the radical particles of NO3 to form C2H4NO3 ads. A further decrease in temperature leads to the fact that the formed NO3 radicals continue to be accepted by the second bond of the active particles of C2H4NO3.

Thus, based on the analysis of the data obtained by the complex of methods, the formation of organic nitrates can be represented as follows [29].

$$C2H4\ NO3\ ads. + NO3\ ads. \rightarrow C2H4(NO3)2 \qquad (12),$$

the current efficiency of which increases with decreasing temperature. Removal of C2H4NO3 ads. from the reaction zone leads to a decrease in the amount of 1,4-butylene glycol dinitrate formed during the recombination of these particles:

$$C2H4\ NO3\ ads. + C2H4\ NO3\ ads. \rightarrow (C2H4)2\ (NO3)2 \quad (13).$$

Simultaneously with the decrease in temperature, a decrease in the EP of butyl nitrate is observed, formed by the mechanism of electrochemical desorption:

$$C2H4\ NO3\ ads. + C2H5COO^{-} - e \rightarrow C4H9\ NO3 + CO2 \quad (14).$$

The CO of ethyl nitrate continues to increase with decreasing temperature. This becomes understandable, since, as shown above, with decreasing temperature, the concentration of carboxylate radicals increases and, consequently, the formation of ethyl nitrate occurs by the recombination reaction:

$$C2H5COO\ ads. + NO3\ ads. \rightarrow C2H5NO3\ ads. + CO2 \qquad (15).$$

Based on the data obtained, it is difficult to predict whether reactions (12, 13, 15) proceed by the mechanism of recombination or electrochemical desorption. However, given the insignificant stabilization of NO3 radicals with decreasing temperature and the different effects of temperature on the CO of individual organic nitrates, it can be assumed that these reactions occur via the recombination mechanism. At the same time, given the high instability of NO3 radicals, the possibility of these reactions occurring by the electrochemical desorption mechanism cannot be excluded.

The obtained regularities can be used to obtain other compounds during the electrolysis of a binary mixture - propionate and salts of inorganic or organic acids.

Conclusion

A significant effect of pH of the medium of both systems (acetate + nitrate - system 1, propionate + nitrate - system 11) on the selectivity of electrochemical reactions is shown. It is established that in acidic solutions of systems 1 and 11, as well as in a slightly alkaline solution of system 1, nitrate ion participates in the process as a source of active oxygen, which goes to the formation of molecular oxygen and the destructive oxidation of alkyl groups of organic compounds. In a weakly alkaline solution of system 11, radical NO3 particles react with ethylene to form an intermediate complex C2H4NO3ads, which then interacts with inorganic and organic radical forms to form organic nitrates. A mechanism for the formation of organic nitrates is proposed.

References

1. Yakovleva AA, Kasatkin EV, Veselovsky VI, Bayramov RK, Vorobey VL (1977) Study of anodic behavior of nitrate ion on platinum in alkaline solutions. Electrochemistry 13: 361-367.
2. Woods R (1959) Limiting oxygen coverage of a smooth platinum anodies in acetate solutions. J. Electroanalyt. Chem. and interfacial Electrochemistry 21: 457-460.
3. Fioshin M Ya, Vasilyev Yu B, Gaginkina EB (1960) On the influence of the cation nature on Kolbe electrosynthesis. Reports of the USSR Academy of Sciences 134: 879-882.
4. Girina GP, Fioshin M Ya, Kazarinov VE (1965) Study of the surface state of a platinum anode at potentials preceding the Kolbe electrosynthesis. Electrochemistry 1: 478-481.
5. Fleischman MK, Mansfield JR, Wohne – Joknes J (1965) The anodic oxidation solutions of acetate ions at smooth platinum electrodes. I. The non-study state of oxidation of platinum. J. Electroanalyt. Chem 10: 511-521.
6. Kazarinov VE, Girina GP (1967) Study of the structure of a double electric layer on platinum in the presence of acetate ions. Electrochemistry 3: 107-110.
7. Vijh AK, Convay BE (1967) Controlled Potential Studies of the Kolbe Reaction and of Coadsorbed Surface Oxide. J. Phys. Chem 71: 3665-3664.
8. Weinberg HR, Weinberg NL (1968) Electrochemical oxidation of organic compounds. Chem. Rev 68: 449-523.
9. Yakovleva AA, Kaidalova SN, Skuratnik Ya B, Veselovsky VI (1972) Adsorption of acetate on smooth platinum at high anodic potentials. Electrochemistry 8: 1799-1802.
10. Fioshin M Ya, Mirkind LA (1972) Application of the method of fixing radicals with an acceptor to study the mechanism of anodic processes involving organic substances. In the collection Catalytic reactions in the liquid phase. Alma-Ata: Science 226-230.
11. Duyunin AG, Mirkind LA, Kazarinov VE, Fioshin M Ya (1974) Study of adsorption of some carboxylic acids on oxidized platinum by radioactive indicator method. In the collection Catalytic reactions in the liquid phase Alma-Ata: Nauka 352-356.
12. Holeman P (1937) Zur Electrolyse deuterium-containing fatty acids, II. Mittel. The mechanism of absorption of the electrons in propionates. Reports of the German Chemical Society 70: 819-827.
13. Kruis A, Schanzer W (1942) Zur Electrolyse deuterium-containing fatty acids. IV. The mechanism of ethane-, butane- and alcohol formation during the electrolysis of propionacid. Zeitschrift for Physical Chemistry 191A: 301-313.
14. Chida K, Sekine T (1970) Anodic processes of aqueous propionic acid and propionate mixture with platinum lead dioxide and graphite anodes. Denki Kagaku = Journal of the electrochemical society of Japan 38: 130-138.
15. Kunugi A, Iseki S, Izumi I, Tanimoto T, Nagaura S (1971) Mechanism of the Propionate Kolbe Electrode Reaction in

Aqueous Medium. Nippon Kagaku Kaishi 92: 768-772.
16. Bayramov RK, Yakovleva AA, Veselovsky VI (1976) Oxidation of propionate ion on platinum at high anodic potentials. Effect of electrolysis conditions on the rate of product formation. Electrochemistry 12: 1870-1873.
17. Fichter F, Siegrist W (1936) Electrolysis of propionate mixtures with nitrates. Helv.chim. Acta 18: 18-25.
18. Fichter F, Metz F (1936) Electrolysis of n-Byte mixtures with nitrates. Helv.chim. Acta 19: 597-606.
19. Fichter F, Lenpin O (1938) Electrolysis of sodium bicarbonate in aqueous solutions with nitrates. Helv.chim. Acta 21: 616-625.
20. Fichter F, Steibuch W (1943) Nitrate – mischelektrolystn with malonsaure, with the sauren outer malonsaure, the ethyl- and diethyl-malonsaure and the bernsteisaure. Helv.chim. Acta 26: 695-704.
21. Likhobolov VA, Ermakov Yu N (1976) Homogeneous catalytic oxidation of olefin oxidation to nitrates of 1,2-glycols in the presence of palladium (11) complexes. Study of the mechanism and kinetics of reactions. Kinetics and catalysis 17: 133-140.
22. Likhobolov VA, Ermakov Yu N (1976) Homogeneous catalytic oxidation of olefins to nitrates of 1,2 diols in the presence of palladium (11) complexes. Study of the composition of the products of interaction of olefins with nitric acid. Kinetics and catalysis 17: 123-133.
23. Svetlov BS, Shelaputina VP (1966) Study of the kinetics of acid hydrolysis of some polynitrates of polyhydric alcohols. Zhurn. Phys. Chem 40: 2889-2891.
24. Bayramov RK (2025) Oxidation of Nitrate Ions at a Platinum Anode. Journal of Engineering and Applied Sciences Technology 7: 1-8.
25. Balashova NA, Kazarinov VE (1965) Study of the structure of the double electric layer on platinum by the method of radioactive indicators. Uspekhi Chem 34: 1721-1732.
26. Pospelova NV, Rakov AA, Veselovsky VI (1969) Study of the surface condition of platinum and rhodium electrodes in sulfuric acid at high anodic potentials by the method of radioactive indicators. Electrochemistry 5: 1318-1320.
27. Potapova GF, Rakov AA, Veselovsky VI (1973) Study of the surface condition of platinum anode in the process of electrochemical low-temperature synthesis of peroxy compounds during electrolysis of a mixture of sulfuric and perchloric acids by the method of radioactive indicators. Electrochemistry 6: 1573-1576.
28. Gerovich MA, Kaganovich RN (1959) Study of the technique of some anodic processes with a combination of electrochemical methods with the method of Labeled atoms. Proceedings of I.V. Conference on Electrochemistry. Moscow: USSR Academy of Sciences 277-281.
29. Bayramov RK, Yakovleva AA, Veselovsky VI (1977) Anodic behavior of nitrate ions at high potentials. II. Mechanism of formation of organic nitrates. Electrochemistry 13: 129-132.