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ELECTRODE REACTIONS OF PHOSPHONIC COMPOUNDS OF ATMP AND HEDP ON A PLATINUM AND GLASS-CARBON ELECTRODES

Abstract. The electrochemical activity of ATMF (aminotrismethylenephosphonic acid) and HEDP(1-hydroxyethane 1,1-diphosphonic acid) in solutions of sodium sulfate in the pH range from 1 to 6 on platinum and glass-carbon disc electrodes was determined. It has been established that as the pH decreases, an increase in the current maximum due to the electroreduction of protonated forms of the investigated phosphonic acids is observed. The current value of the cathode maximum for ATMF and HEDP at a constant pH of the solution 3: 2, which corresponds to the ratio of the phosphonic groups in these compounds. On the glass- carbon electrode in the process of anodic polarization, an anode wave is observed for ATMF, which is not characteristic of HEDP under similar experimental conditions. The obtained regularities can be used to determine the ATMF by change in current value of the anode peak from the concentration in the solution study.

Keywords: anodic dissolution, cyclic voltammetry, cathodic maximum, initial potential, potential sweep rate.

Introduction. There are numerous data in the literature on the use of complexones of NTF, OEDP and their complexonates with metal ions as inhibitors of salt formation and corrosion on metals and alloys of different nature [1-16]. Along with the positive effect on the use of these compounds to prevent corrosion and scaling, there is information about the negative consequences of these compounds. The last one is associated not only with technical problems of their operation in real conditions, but also to a greater extent with the absence of a serious fundamental basis for establishing the electrochemical activity of these compounds in neutral and close to neutral solutions on electrodes of different nature and pH. In this connection, special importance is given to establishing the regularities of electrochemical reactions on indifferent disk electrodes made of platinum and glassy carbon.

Experimental method. Cyclic volt-ampere curves were obtained at the potentiostat-galvanostat AUTOLAB (Netherlands) in a sealed cell with a thermostated at 250 ° C using a LOIPLT-105 (Russia) thermostat. The working electrodes were a disk, platinum and glassy carbon electrode with a visible surface of 0.03 cm². To update the surface of the working electrode, abrasive paper of the brand MIRKA 2000 (Finland) was used when the electrode was rotated at 2500 rpm, followed by washing with distilled water. The auxiliary electrode was a platinum helix with a visible surface exceeding the surface of the working electrode by more than 100 times. The potentials given in the article were measured with respect to silver chloride electrode from Metrohm (Switzerland) with a potential of 198 mV relative hydrogen electrode. Deaeration of the volume of the solution in the cell was carried out with an inert gas of argon "v.h." Measurement of the pH of the solution was carried out using a pH-meter of pH-150MI (Russia). Distilled water was used to prepare the solutions. The reagents Na₂SO₄, NTF and OEDF used in the work had qualifications "hh" and "o.ch."

Results and its discussion. Figure 1 shows cyclic volt-ampere curves on a platinum electrode in a solution of 0.3M Na₂SO₄ for various concentrations of NTF at a constant pH of 5.6 in the potential range from -0.4 to -0.8V. Volt-ampere curves were taken in the following order. Initially, cathode volt-ampere

curves were obtained from the initial potential of -0.4V to a final potential of -0.8V , followed by a reversal of the potential sweep to the opposite direction. Anode volt-ampere curves were recorded at the same time. According to Figure 1 in the presence of NTF (CNTF = $1.99 \cdot 10^{-4}\text{ M}$), the cathode current peak at $E \sim -0.65\text{ V}$ and the anode maximum at $E \sim -0.57\text{ V}$ are observed at the cathode and anode parts of the current-voltage curves. As the concentration of NTF increases, the cathode peak of the current shifts to the region of more negative potentials, and the anode maximum to the region of more positive potentials.

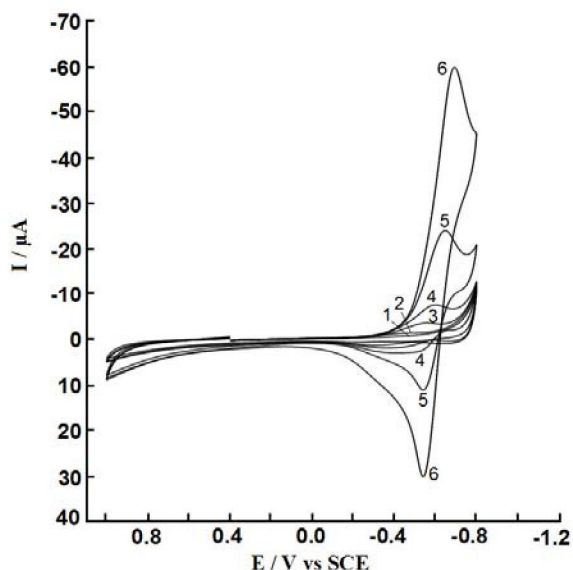


Figure 1 – Cyclic volt-ampere curves of a platinum electrode in a solution of $0.3\text{ M Na}_2\text{SO}_4$ in the presence of different concentrations of NTF. The electrolyte is $0.3\text{ M Na}_2\text{SO}_4$; $\text{pH} = 5.6$; concentration of NTF (M): 1 – 0; 2 – $1.99 \cdot 10^{-4}$; 3 – $6.95 \cdot 10^{-4}$; 4 – $1.67 \cdot 10^{-3}$; 5 – $5.39 \cdot 10^{-3}$; 6 – $1.36 \cdot 10^{-2}$

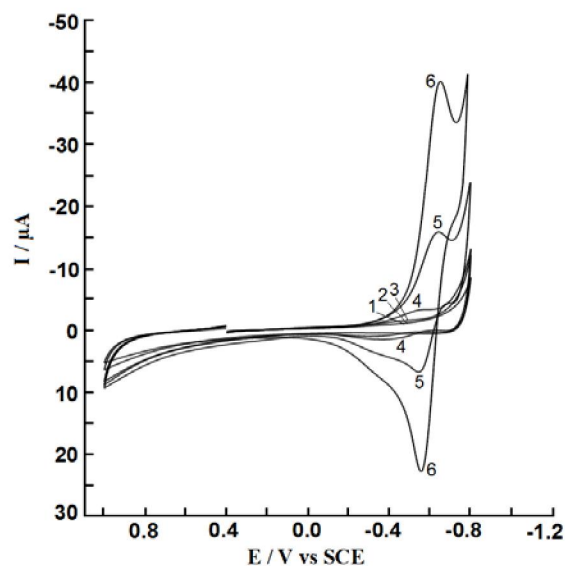


Figure 2 – Cyclic volt-ampere curves of a platinum electrode in a solution of $0.3\text{ M Na}_2\text{SO}_4$ in the presence of different concentrations of OEDPH. The electrolyte is $0.3\text{ M Na}_2\text{SO}_4$; $\text{pH} = 5.6$; concentration of OEDPH (M): 1 – 0; 2 – $1.99 \cdot 10^{-4}$; 3 – $6.95 \cdot 10^{-4}$; 4 – $1.67 \cdot 10^{-3}$; 5 – $5.39 \cdot 10^{-3}$; 6 – $1.36 \cdot 10^{-2}$

In many respects similar volt-ampere curves under similar conditions were obtained for Oxyethylidenediphosphonic acid. Cyclic voltammetric curves on a platinum electrode in a solution of $0.3\text{ M Na}_2\text{SO}_4$ for different concentrations of Oxyethylidenediphosphonic acid ($\text{pH} = 5.6$) are shown in Figure 2. Comparing the cyclic voltammetric curves for identical concentrations of Nitrilotrimethylphosphonic acid and Oxyethylidenediphosphonic acid, it follows that the value of the current of the cathode maxima for the investigated phosphonates is significantly different. The current ratio of the maxima for NTPH and OEDPH at the same concentrations is 3:2, which corresponds to the ratio of the phosphonic groups in NTPH and OEDPH. In other words, the magnitude of the current of the maxima on the cathode and anode volt-ampere curves is determined by the presence of phosphonic groups, provided that the pH of the solution does not change.

The magnitude of the current of the maxima and the shape of the curves on cyclic voltammograms is largely determined by the pH of the solution. This is clearly seen from Figure 3, which shows cyclic volt-ampere curves on a platinum electrode in a $0.3\text{ M Na}_2\text{SO}_4$ solution in the presence of different concentrations of NTF at $\text{pH} = 3.0$. This is clearly seen from Figure 3, which shows cyclic volt-ampere curves on a platinum electrode in a $0.3\text{ M Na}_2\text{SO}_4$ solution in the presence of different concentrations of NTPH at $\text{pH} = 3.0$.

According to Figure 3, with an increase in the concentration of NTPH at a constant $\text{pH} = 3.0$, the shape of the current-voltage curves varies significantly. Thus, if in the solution of $0.3\text{ M Na}_2\text{SO}_4$ in the absence of NTF (Figure 3, curve 1), the cathodic and anodic current peaks are observed on the cyclic voltammetric curves, then in the presence of NTPH the shape of the maxima changes significantly. On the cathode part of the current-voltage curve (Figure 3, curve 2), along with a small current maximum at $E = -0.45\text{V}$, one more current maximum is observed for more negative values of the potential $E = -0.65\text{V}$.

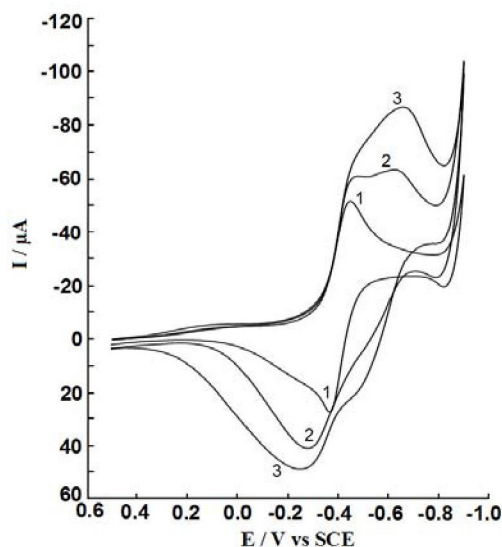


Figure 3 –
Cyclic volt-ampere curves of a platinum electrode
in a solution of 0.3 M Na₂SO₄
in the presence of different concentrations of NTPH.
Electrolyte 0.3 M Na₂SO₄; pH = 3;
concentration of NTPH (M):
1 – 0; 2 – 3.85 · 10⁻³; 3 – 7.4 · 10⁻³

On curve 3 (Figure 2), the current maximum at E = -0.45V is practically not observed, but the current of the maximum at E = -0.65V appreciably increases.

The appearance of the maximum current on curve 1 (Figure 3) in a solution of 0.3 M Na₂SO₄ at E = -0.5 V can be explained by the depletion of the near-electrode layer by H⁺ hydrogen ions as a result of their electroreduction and, as a consequence, an increase in pH in the near-electrode space platinum electrode, then on curves 2,3 (Figure 3), similar phenomena are manifested to a lesser extent due to the presence in the solution and in the near-electrode space of protonated forms of NTPH in the mobile equilibrium, which may be one of the reasons for a significant change in the pH of the near-electrode layer. The protonation constants for NTPH have the following values [17]:

Protonation constants for NTPH and HEDPH

Complexes	$\frac{[HL]}{[L][H^+]}$	$\frac{[H_2L]}{[HL][H^+]}$	$\frac{[H_3L]}{[H_2L][H^+]}$	$\frac{[H_4L]}{[H_3L][H^+]}$	$\frac{[H_5L]}{[H_4L][H^+]}$	$\frac{[H_6L]}{[H_5L][H^+]}$
N(CH ₂ PO ₃ H ₂) ₃	12,10	7,30	5,86	4,64	1,50	0,30
CH ₃ (OH)C(PO ₃)H ₂	10,23	7,28	2,47	–	–	–

In Figure 4, cyclic voltammetric curves are compared on a platinum electrode for solutions with different pH values and a constant concentration of NTPH. According to Figure 4, the magnitude of the current of the maxima on cyclic voltammetric curves varies significantly with different pH. Thus, in a solution close to neutral (pH = 8.4), the cathodic and anodic current maxima are practically absent in cyclic voltammetric curves. However, even at pH = 5.6 on the current-voltage curves, current maxima clearly manifest. In an acidic medium pH = 3.0, a sharp increase in current is observed at the cathode and anode parts of the current-voltage curves. If at pH = 5.6 the potential difference between the cathode and anode peaks is ~ 80 mV, then at pH = 3.0 this value is 200 mV.

It was interesting to clarify the effect of zinc ions on the current-voltage curves obtained on a platinum electrode in a solution of 0.3 M Na₂SO₄ (Figure 5, curve 1) containing a constant concentration of NTPH (Figure 5, curve 2) and in the presence of different concentrations of zinc ions (Figure 5, curves 3,4) in solutions close to neutral with pH = 5.6 and in acidic solutions (pH = 3). According to Figure 5a, when the concentration of zinc ions in a solution of 0.3 M Na₂SO₄ + 3.85 · 10⁻³ M NTPH is increased at a constant pH of 5.6, the magnitude of the current of the cathodic and anodic maxima on cyclic voltammetric curves increases significantly, which can be associated with the formation of complex compounds between zinc ions and NTPH.

In acidic solutions (pH = 3.0), the observed phenomenon is manifested to a lesser extent. An increase in the concentration of zinc ions (Figure 5b) leads to an insignificant increase in the current of a weakly

Figure 4 –
Cyclic volt-ampere curves of a platinum electrode
in solutions with different pH values,
in the presence of a constant concentration
of NTF ($3.85 \cdot 10^{-3}$ M).
The electrolyte is 0.3 M Na_2SO_4 ;
1 – pH = 3; 2 – pH = 5.6; 3 – pH = 8.4

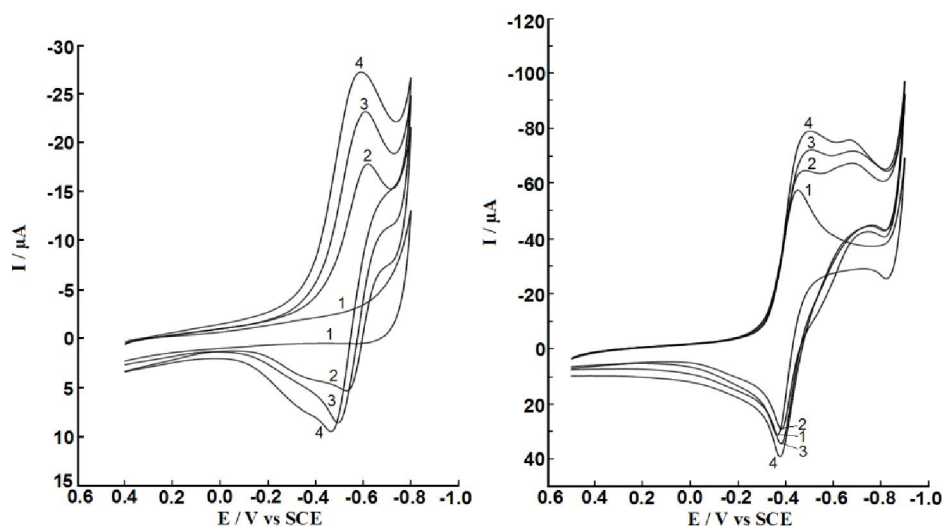
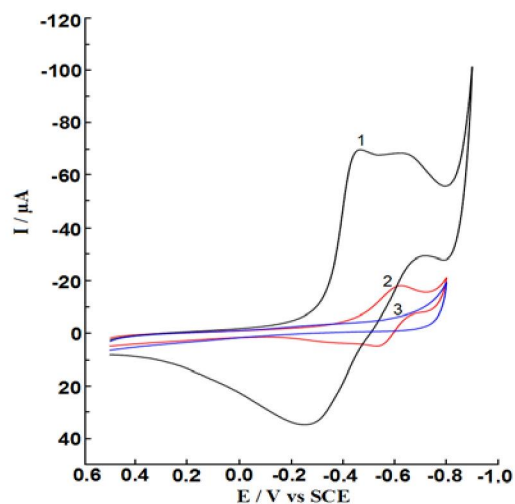


Figure 5 – Cyclic volt-ampere curves of a platinum electrode in a solution of 0.3 M Na_2SO_4 containing a constant concentration of NTF ($3.85 \cdot 10^{-3}$ M) with pH 5.6 (a) and pH 3 (b) in zinc ions:

1 – background 0.3 M Na_2SO_4 ; 2 – 0.3 M Na_2SO_4 + $3.85 \cdot 10^{-3}$ M NTF;
3 – 0.3 M Na_2SO_4 + $3.85 \cdot 10^{-3}$ M NTF + $2.91 \cdot 10^{-3}$ M ZnSO_4 ; 4 – 0.3 M Na_2SO_4 + $3.85 \cdot 10^{-3}$ M NTF + $4.76 \cdot 10^{-3}$ M ZnSO_4

expressed maximum, without significantly affecting the course of the cathode volt-ampere curves. The observed phenomenon is evidently due to the fact that complex compounds are formed in acid solutions between protonated forms of NTPH and zinc ions. The lack of substitution of protons for metal ions with NTPH can lead to the formation of MHL, MH₂L and MH₃L [18, 19].

In order to elucidate the influence of the nature of the electrode material on electrode reactions involving NTPH and OEDPH, a glassy carbon disc electrode was used along with the platinum disc electrode. Figure 6a shows the current-voltage curves on a glassy carbon electrode in a solution of 0.3 M Na_2SO_4 (pH = 5.6) for various concentrations of NTPH, the concentration of which varied from $1.99 \cdot 10^{-4}$ to $1.36 \cdot 10^{-2}$ M. Cyclic volt-ampere curves were taken from the initial potential $E_h = -0.14$ to $E_k = -1.4$ V with the subsequent reversal of the direction of the potential swing to + 1.2 V. When this potential was reached, the curve was taken from + 1.2 V to -0.14 V. According to Figure 6, at the cathode part of the current-voltage ones, in contrast to the platinum on the glassy carbon electrode, the maximum current of the electric reduction of hydrogen ions and the effect on this process of NTPH is practically not observed. However, in the potential range from 0.5 to 1.1 V, an anodic wave with a clearly pronounced maximum is observed whose current value depends on the concentration of NTPH. It should be noted that similar phenomena on the platinum electrode under similar conditions are not observed.

Figure 6b shows the cyclic volt-ampere curves for OEDPH under similar conditions of the range of the potential for the removal of cyclic voltammetric curves, the pH of the solution and the selected concentrations.

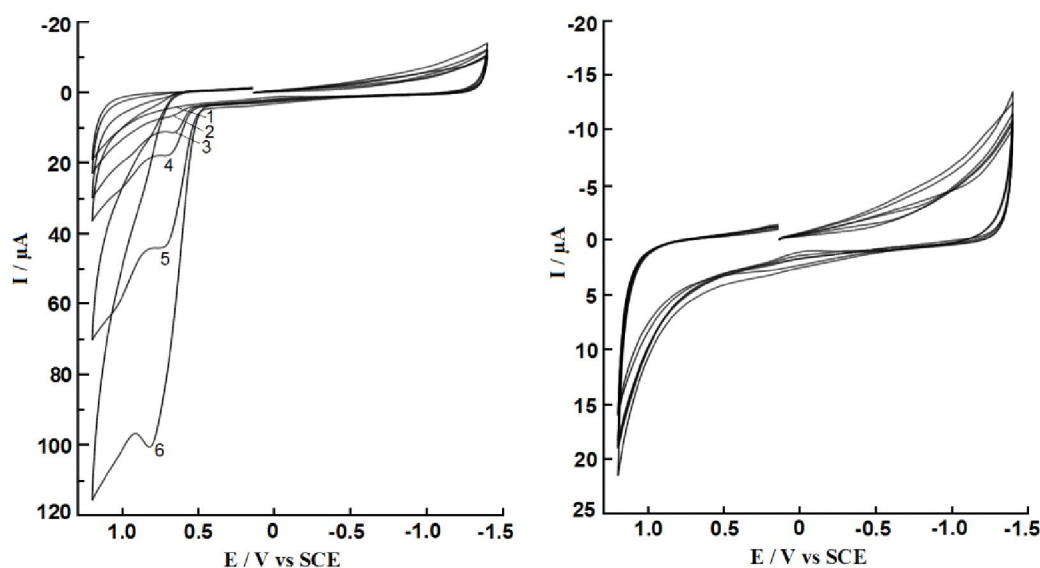


Figure 6 – Cyclic voltammetric curves on a glassy carbon electrode in a solution of 0.3 M Na_2SO_4 in the presence of different concentrations of NTPH (a) and OEDPH (b). Electrolyte 0.3 M Na_2SO_4 ; pH = 5.6; concentration of NTPH and OEDPH (M): 1 – 0; 2 – $1.99 \cdot 10^{-4}$; 3 – $6.95 \cdot 10^{-4}$; 4 – $1.67 \cdot 10^{-3}$; 5 – $5.39 \cdot 10^{-3}$; 6 – $1.36 \cdot 10^{-2}$

According to Figure 6b, in the presence of OEDPH on the cathodic and anodic part of the cyclic voltammetric curves, maximum current is not observed in the potential range studied. In other words, the glassy carbon electrode is not indifferent to nitriles and can be used to determine NTPH in solutions containing other phosphonic compounds [20].

Conclusions. Thus, using a disk electrode from platinum, it was possible to establish the electrochemical activity of the phosphonic compounds of NTPH and OEDPH, which are determined by the presence of protonated phosphonic groups. The current of electroreduction of these compounds in solutions with pH = 5.6 is determined by the ratio 3: 2, which corresponds to the presence of three protonated forms in NTPH and two in OEDPH. The influence of zinc ions on the change in the current of electroreduction of protonated forms of NTPH in acid solutions and solutions close to neutral has been established. In solutions with pH 5.6 in the presence of Zn ions, an increase in the maximum current is observed due to a change in pH as a result of exchange reactions between the protonated form of NTF and zinc ions with the formation of ZnNTPH , and in acidic solutions such phenomena are not observed due to the formation of protonated complexes. The electrochemical activity of NTPH and OEDPH on a glassy carbon electrode was established. NTPH, in contrast to OEDPH, is able to participate in anodic reactions due to the presence of nitrile groups in NTPH. The presence of protonated forms for NTPH and OEDPH under the cathodic polarization of the glassy carbon electrode on the current-voltage curves does not appear in the form of current maxima.

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ЭЛЕКТРОДНЫЕ РЕАКЦИИ ФОСФОНОВЫХ СОЕДИНЕНИЙ НТФ И ОЭДФ НА ПЛАТИНОВОМ И СТЕКЛОУГЛЕРОДНОМ ЭЛЕКТРОДАХ

Аннотация. Определена электрохимическая активность НТФ (нитрилотриметиленфосфоновая кислота) и ОЭДФ (оксиэтилендифосфоновая кислота) в растворах сульфата натрия в интервале рН от 1 до 6 на платиновом и стеклоуглеродном дисковых электродах. Установлено, что с уменьшением рН наблюдается увеличение максимума тока, обусловленного электровосстановлением протонированных форм исследуемых фосфоновых кислот. Величина тока катодных максимумов для НТФ и ОЭДФ при постоянном рН раствора соотносятся 3:2, что соответствует отношению фосфоновых групп в этих соединениях. На стеклоуглеродном электроде в процессе анодной поляризации наблюдается анодная волна для НТФ, которая не характерна для ОЭДФ в аналогичных условиях эксперимента. Полученные закономерности могут быть использованы для определения НТФ по изменению величины тока анодного максимума от концентрации в исследуемом растворе.

Ключевые слова: анодное растворение, циклическая вольтамперометрия, катодный максимум, начальный потенциал, скорость развертки потенциала.

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ПЛАТИНА ЖӘНЕ ШЫНЫ КӨМІРТЕКТІ ЭЛЕКТРОДТАРДАҒЫ НТФ ЖӘНЕ ОЭДФ ФОСФОНДЫ ҚОСЫЛЫСТАРЫНЫҢ ЭЛЕКТРОДТЫҚ РЕАКЦИЯЛАРЫ

Аннотация. Дискілі платина және шыны-көміртекті электродтарда рН мәні 1 мен 6 аралығындағы натрий сульфаты ерітінділерінде НТФ (нитрил үшметилді фосфонды қышқыл) және ОЭДФ (оксиэтилен дифосфонды қышқыл) тың электрохимиялық белсенділігі анықталынды. рН мәнінің төмендеуіне байланысты зерттелінетін фосфонды қышқылдардың протонды формаларының электрототықсыздануы кезінде пайда болатын максимумының ток мөлшері артатындығы зерттелінді. Ерітіндінің тұрақты рН мәндерінде НТФ пен

ОЭДФ тың катодтық максимумдарының тоғының шамасы осы қосылыстардағы фосфонды топтардың арақатынасына сәйкес келетін 3:2 қатынасын құрайды. Тәжірибені өткізудің бірдей жағдайларында шыныкөміртек электродында анодты поляризация кезінде НТФ-ті қосқанда анодтық толқын пайда болады бірақ ОЭДФ тың қатысында мұндай құбылыс байқалмайтындығы зерттелінді. Алынған заңдылықтар зерттелінген ерітінділерде анодтық максимумдардың ток шамасының концентрацияға байланысты өзгеруі бойынша НТФ ты анықтауға қолданылуы мүмкін.

Түйін сөздер: анодтық еру, циклді-вольтамперометрия, катодты максимум, бастапқы потенциал, потенциал беру жылдамдығы.

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