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# Electrochemical Behavior of Ti(IV)/Ti(III) Redox Couple on Dropping Mercury Electrode in Sulfuric Acid Aqueous and Aqueous-Organic Media

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**Abstract**—The processes of electrochemical reduction of Ti(IV) and oxidation of Ti(III) in aqueous solutions of $H_2SO_4$ not containing and containing AcOH or MeCN are studied by the methods of classical and commutation polarography. It is shown that in the absence of organic solvents the heterogenous electron transfer is irreversible in the media with the sulfuric acid concentration up to 9 M, while in aqueous-organic solution the same occurs at the concentration up to 7 M. Organic solvents are involved into the process of complex formation and like $H_2SO_4$, influence the step of heterogenous electron transfer; this effects weakens with the increase in the concentration of sulfuric acid.

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Solutions of sulfuric acid containing Ti(IV) are used in the processes of indirect cathode synthesis of primary amines [1–6]. The Ti(IV)/Ti(III) couple operates as a mediator system, therefore the efficiency of reduction of nitro compounds [1–4] and radical amination of unsaturated and aromatic substrates [5, 6] depends on its oxidation–reduction properties that are defined at the given temperature by the electrolyte composition. In this work by the methods of classical and reverse polarography we estimated the effect of acetic acid and acetonitrile, the organic compounds used in radical synthesis of amino compounds [5–7], on the electrochemical behavior and redox potential of the couple Ti(IV)/Ti(III) in aqueous solutions of $H_2SO_4$.

*Aqueous solutions of sulfuric acid.* Polarographic behavior of titanium ions was studied in $H_2SO_4$ solutions of 1 to 11 M concentration. The upper and lower concentration limits were chosen accounting for the stability of Ti(IV) solutions under the conditions of amination [5, 6] and DME (dropping mercury electrode) in sulfuric acid electrolytes [8].

At the aqueous solution concentration 1–1.5 M $H_2SO_4$ in the polarograms of classical reduction of 0.001 M Ti(IV) two waves are registered (Table 1, Fig. 1), no. 1 and no. 2. The height of the poorly expressed first wave increases with the increase in the acid concentration.

Electrochemical reduction of titanium(IV) at the potentials of both these waves proceeds irreversibly. The irreversibility of the electron transfer follows from the angular coefficients of classical waves (tan β) that are considerably higher than 60 mV (Table 1), existence anodic and cathodic waves in the polarigrams recorded with the Ist commutation scheme (Fig. 1), as well as the absence of anodic current at the commutation by the IInd scheme from the potentials of the foot of waves no. 1 and no. 2 (in the case of curve *4,* solid line). Limiting currents of both first ($I_{lim1}$), and second ($I_{lim2}$) waves are of kinetic nature because the ratios $I_{lim1}/t^{1/6}$ and $I_{lim2}/t^{1/6}$ are the functions of dropping period (Table 1). The occurred difference in halfwave potentials ($E_{1/2}$) in the voltammograms of Ti(III) oxidation in classical and commutation modes (10–20 mV) attest to the favor of probable change in time of the composition of cathode-generated Ti(III) complexes.

On the basis of the published data on the composition of Ti(IV) complexes in the sulfuric acid solutions [9] and accounting for the results of investigations carried out recently with the solutions of sulfuric and perchloric acids [10], the first Ti(IV)

**Table 1.** Electrochemical parameters of some typical classical polarograms of Ti(IV) reduction in sulfuric acid solutions; $C_{Ti(IV)}$ =0.001 M, $T$ = 25°C

| $C(H_2SO_4)$, M | $t$, s | $-I_{lim}$, μA | $E_{1/2}$, mV | tan β, mV | $-I_{lim}/t^{1/6}$, μA $s^{-1/6}$ | $-I_a/I_{lim}$ [a] |
|---|---|---|---|---|---|---|
| 1.5[b] | 0.31 | 0.390 | –265 | 185 | 0.47 | ~0 |
| | 0.51 | 0.455 | –255 | 190 | 0.51 | |
| | 0.77 | 0.564 | –245 | 185 | 0.59 | |
| | 1.03 | 0.717 | –240 | 190 | 0.71 | |
| | 0.31 | 2.66 | –810 | 150 | 3.23 | 0 |
| | 0.51 | 3.06 | –805 | 150 | 3.42 | |
| | 0.77 | 3.43 | –795 | 155 | 3.58 | |
| | 1.03 | 3.65 | –790 | 155 | 3.63 | |
| 5 | 0.31 | 2.16 | –105 | 215 | 2.63 | 0.88 |
| | 0.51 | 2.50 | –90 | 190 | 2.80 | |
| | 0.77 | 2.85 | –75 | 175 | 2.98 | |
| | 1.03 | 3.15 | –65 | 165 | 3.13 | |
| 7 | 0.30 | 1.87 | 40 | 70 | 2.27 | 0.95 |
| | 0.51 | 2.06 | 40 | | 2.30 | |
| | 0.75 | 2.22 | 40 | | 2.33 | |
| | 1.02 | 2.35 | 45 | | 2.34 | |
| 9 | 0.31 | 1.51 | 100 | 60 | 1.83 | 1 |
| | 0.51 | 1.63 | | | 1.82 | |
| | 0.77 | 1.74 | | | 1.82 | |
| | 1.03 | 1.84 | | | 1.83 | |

[a] $I_a$ is limiting anode current in the polarogram commutated along the IInd scheme from the potentials of the classical wave foot, $I_{lim}$ is limiting current of the classical wave. [b] In 1.5 M $H_2SO_4$ two waves are registered, no. 1 and no. 2.

reduction wave in 1–1.5 M $H_2SO_4$ can probably be assigned to the reduction of titanyl ions containing in their coordination sphere the sulfuric acid anions, the second wave, to the reduction of the titanyl ions and Ti(IV) hydroxocomplexes.

The increase in $H_2SO_4$ concentration above 1.5 M leads to further increase in the contribution of the first wave to the total height of the classical polarogram (in 2 M acid the waves no. 1 and no. 2 are approximately equal by height) and to the shift of the Ti(IV) reduction waves to the region of lesser cathodic potentials, more significant for the wave no. 2. Besides, a poorly expressed splitting of the first wave into two waves occurs (no. 1a and no. 1b) and a change in the appearance of commutated voltammograms (Fig. 2). This situation leads to restriction in accurate treatment of classical waves due to the absence of clear plateau of limiting current.

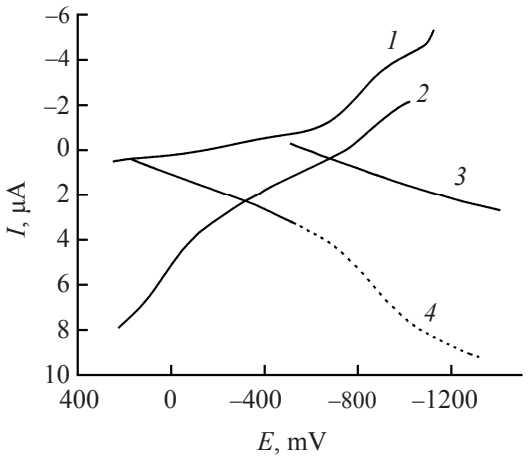


**Fig. 1.** Polarographic waves of 0.001 M Ti(IV) in 1.5 M $H_2SO_4$, recorded in (*1*) classical regime and with commutation by (*2*) Ist and (*3, 4*) IInd schemes; $t$ = 0.51 s.

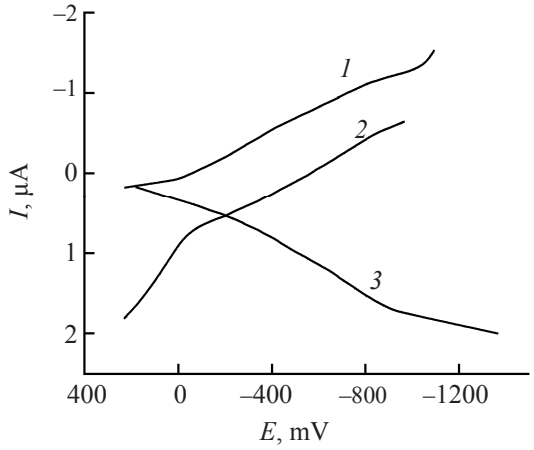


**Fig. 2.** (*1*) Classical and commutated according to (*2*) Ist and (*3*) IInd schemes polarograms of 0.001 M Ti(IV) in 3 M $H_2SO_4$. At the registration of these waves $m$ = 0.86 mg $s^{-1}$, $t$ = 0.51 s.

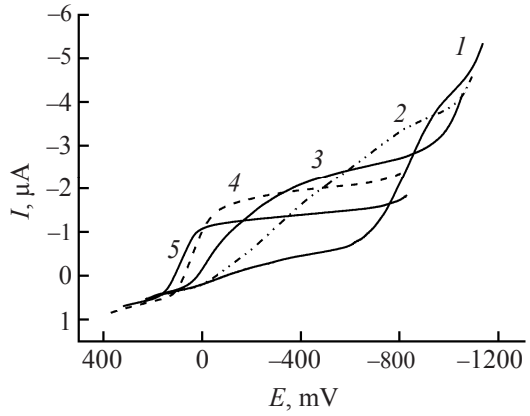


**Fig. 3.** Classical polarograms of Ti(IV) reduction in (*1*) 1, (*2*) 3, (*3*) 5, (*4*) 7, and (*5*) 9 M $H_2SO_4$; $t$ = 0.51 s.

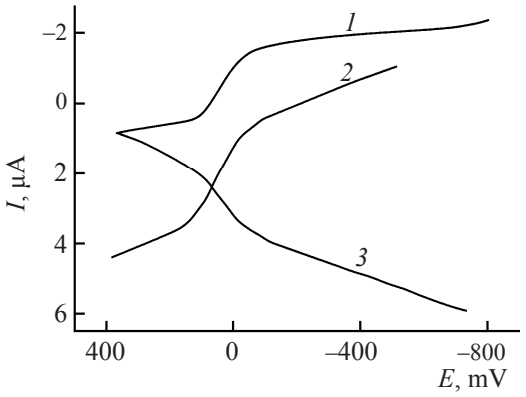


**Fig. 4.** (*1*) Classical and commutated by (*2*) Ist and (*3*) II schemes voltammograms of 0.001 M Ti(IV) in 7 M $H_2SO_4$; $t = 0.51$ s.

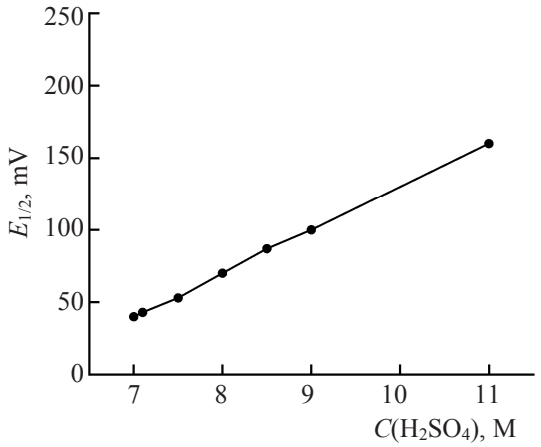


**Fig. 5.** Plot of $E_{1/2}$ of the wave of Ti(IV) reduction [Ti(III) oxidation] on the sulfuric acid concentration.

In the polarograms recorded for 4–5 M $H_2SO_4$ one Ti(IV) reduction wave is registered sloping more gently in the upper part (Fig. 3, curve *3*) that mostly represents a sum of the waves no. 1a and no. 1b, smoothly passing one into another at the change in DME potential.

Further increase in the acid content in solution leads to a shift of Ti(IV) reduction and Ti(III) oxidation waves to higher anodic potentials, with the rapprochement of their half-wave potentials and decrease in tan β. The wave heights fall first of all due to the increase in the medium viscosity.

In 7 M $H_2SO_4$ the nature of limiting current of Ti(IV) reduction is close to diffusion and the electron transfer is quasi-reversible. Therefore the half-wave potentials of oxidized and reduced forms of the Ti(IV)/Ti(III) redox couple practically coincide (Fig. 4), but tan β value remains above 60 mV (Table 1).

The electrode process becomes reversible in 9 M $H_2SO_4$. According to the data presented in Table 1 and in Fig. 5, the redox potential of Ti(IV)/Ti(III) couple that in a first approximation corresponds to $E_{1/2}$ of the reversible wave of Ti(IV) reduction [11], grows with the increase in sulfuric acid concentration. Basing on the data [10] it is presumable that in solutions with high content of sulfuric acid the Ti(IV) complexes are reduced containing hydrosulfate anions in the coordination sphere. (One of our nearest future work will concern a more accurate establishing the composition of Ti(IV) complexes in aqueous $H_2SO_4$.

In the above experiments Ti(III) is not consumed in the subsequent chemical reactions. Hence in the absence of specific adsorption of titanium ions on DME the ratio of total limiting current in the polarogram at the commutation according to IId scheme at the potential of the limiting current of Ti(III) oxidation ($I_a^{\Sigma}$) to the total limiting current in the classical polarogram ($I_{lim}^{\Sigma}$) can be taken as a measure of efficiency of cathodic generation of Ti(III). Therefore for the registration of common anodic waves in the media with low $H_2SO_4$ content (Fig. 1, curve *4* including the dotted line) and accurate estimation of the $-I_a^{\Sigma}/I_{lim}^{\Sigma}$ ratio we used the DME potentials for the working half-cycle of IInd scheme after the registration of the polarograms commutated according to Ist scheme (the potentials of foot of the first classical half-wave are close to the potentials of limiting current of Ti(III) oxidation only in the media with the acid concentration 4 mol $l^{-1}$ and higher). In 1–1.5 M $H_2SO_4$ solutions the $-I_a^{\Sigma}/(I_{lim1} + I_{lim2})$ is 0.72–0.75. These data and the results listed in Table 1 show that the increase in the acid concentration favors the process of electrochemical reduction of Ti(IV); the efficiency of Ti(III) generation reaches unity in 9 M $H_2SO_4$ (Table 1).

Our data of the polarographic behavior of Ti(IV)/Ti(III) couple in aqueous solutions of sulfuric acid are consistent with those published in [9, 10, 12, 13], and the character of the influence of $H_2SO_4$ concentration on the efficiency of electrochemical generation of Ti(III) is consistent with the earlier reported results obtained with DME [12, 13], platinum [14], and copper [15] electrodes.

*Acidic aqueous–organic media.* Adding of organic solvents to the aqueous solution of 1 M $H_2SO_4$ leads to

**Table 2.** Electrochemical parameters of classical waves of Ti(IV) reduction in 1 M $H_2SO_4$ solutions. $C_{Ti(IV)}$ = 0.001 M, $t$ = 0.51 s.

| $C$(AcOH), M | Wave no. 1[a] | | | Wave no. 2 | | |
|---|---|---|---|---|---|---|
| | $-I_{lim}$, μA | $-E_{1/2}$, V | tan β, V | $-I_{lim}$, μA | $-E_{1/2}$, mV | tan β, mV |
| 0 | 0.17 | 0.21–0.26 | 0.15–0.20 | 3.17 | 835 | 140 |
| 1 | 0.20 | 0.12–0.16 | – | 3.04 | 850 | 130 |
| 3 | 0.26 | 0.05–0.07 | – | 2.75 | 875 | 115 |
| 5 | 0.30 | 0.045 | 0.100 | 2.57 | 885 | 115 |

[a] In the absence of organic solvent or at its low concentration the accurate estimation of $E_{1/2}$ and tan β of the wave no. 1 is restricted (Fig. 6).

**Table 3.** Effect of acetic acid concentration on the ratio $-I_a^{\Sigma}/I_{lim}^{\Sigma}$ and on the heights of first and second waves of voltammogram commutated along the IInd scheme, in 1 M $H_2SO_4$ solutions.

| $C$(AcOH), M | $-I_a^{\Sigma}/I_{lim}^{\Sigma}$ | $I_{a1}$, μA | $I_{a2}$, μA | $I_{a2}/I'_{a2}$ |
|---|---|---|---|---|
| 0 | 0 | ~0 | 0 | – |
| 1 | 0.71 | 0.12 | 0.24 | 0.11 |
| 3 | 0.88 | 0.51 | 0.45 | 0.21 |
| 5 | 0.88 | 0.60 | 0.52 | 0.27 |

[a] $I'_{a2}$ is limiting current of second anodic wave registered at the commutation along the IInd scheme from the potentials of limiting current of Ti(III) oxidation.

a significant change in the appearance of the polarograms (Fig. 6). In the presence of AcOH the wave no. 1 grows and undergoes a shift to the region of lesser cathodic potentials. The wave no. 2 decreases and despite smaller value of $H_2O/H_2SO_4$ mole ratio in the aqueous-organic solution as compared with aqueous medium undergoes a shift in the more cathodic region (Table 2, Fig. 6). The values of tan β of the waves are changed, and anodic waves appear at the commutation according to IInd scheme from the potentials of both foots of the waves nos. 1 and 2, the heights of the commutated waves are respectively $I_{a1}$ and $I_{a2}$ (Table 3). It is also noteworthy that at the increase in $CH_3COOH$ concentration in the solution the limiting current $I_{a2}$ grows faster than related current $I'_{a2}$, registered at the commutation from the potentials of the limiting current of Ti(III) oxidation. The presence of a second organic solvent, MeCN, even more affected the electrochemical behavior of Ti(IV)/Ti(III) couple. In particularicular, the wave no. 2 undergoes a shift to more cathodic potentials and even is overlapped by the wave of hydroxonium ions reduction (Fig. 6).

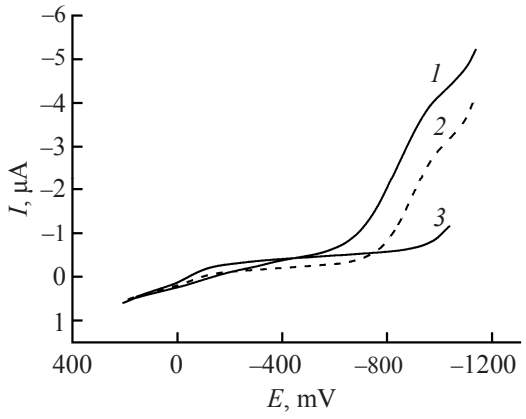


**Fig. 6.** Classical voltammograms of Ti(IV) reduction in 1 M $H_2SO_4$ (*1*) in the absence and in the presence of (*2*) 5 M AcOH or (*3*) 5.5 M MeCN; $t$ = 0.51 s.

Analysis of the polarograms obtained in the aqueous and aqueous-organic 1 M $H_2SO_4$ solutions certainly indicates the change in the coordination spheres of titanium(IV) and titanium(III) complexes at the appearance of AcOH or MeCN in the sulfuric acid solution.

For more detailed estimation of the effect of the nature and concentration of organic solvent on the processes of heterogenous electron transfer, we recorded in this work voltammograms in aqueous-organic media with a constant at first approximation value of $H_2O/H_2SO_4$ mole ratio, corresponding to the mole ratio in aqueous solution of 1 M $H_2SO_4$. The compared pairs of electrolytes contained equal volume concentrations of acetonitrile or acetic acid, therewith molar concentrations of organic solvent differed approximately by 10%. The electrolytes containing MeCN or AcOH were prepared from the 0.001 M solution of Ti (IV) in 1 M $H_2SO_4$ that was used at the registration of voltammograms in the absence of organic solvents, therefore at the increase in organic solvent concentration the concentration of metal ions decreased.

Addition of AcOH or MeCN to the sulfuric acid solution leads to a change in the morphology of both classical and commutation voltammograms (Table 4, Fig. 7). The first waves of classical polarograms despite decrease in Ti(IV) concentration increase and undergo a shift to the lesser cathodic potentials, therewith the values of tan β decrease (Table 4). The

second waves are registered at highe cathodic potentials. Waves appear at the commutation according to IInd scheme, the ratios $-I_a^{\Sigma}/I_{lim}^{\Sigma}$ and $I_{a2}/I'_{a2}$ increase. For example, in the media containing 8 M AcOH these ratios reach values 0.85 and 0.32, respectively. The character of the changes in the electrochemical parameters on voltammograms at the increase in AcOH or MeCN concentration indicate that the solvent molecules (in the case of acetic media probably also acetate ions) are involved into the complex formation and that the portion of Ti(IV) complexes is reduced at the first wave potential grows.

Of these two organic solvents, AcOH and MeCN, the second one affects stronger the step of heterogenous electron transfer at the potentials of both first and second waves (Table 4, Fig. 7).

To obtain the general understanding of electrochemical properties of Ti(IV)/Ti(III) system in the sulfuric acid aqueous-organic media we studied behavior of titanium ions in the solutions with varied content of $H_2SO_4$ and fixed concentration of AcOH or MeCN, commonly applied in the processes of amination of aromatic compounds: 5 M and 5.5 M, respectively [6, 7]. Some results of this study are shown in Tables 5, 6 and Fig. 8.

When the electrolyte contains 5 M AcOH at the increase in sulfuric acid concentration a maximum appears in the voltammogram at the potential of the first wave (its nature here is not considered), and wave no. 2 is shifted to lesser cathodic potentials, its height decreases and tan β increases (Table 5). The maximum

**Table 4.** Parameters of classical polarograms of Ti(IV) reduction in solutions with constant $H_2O$ : $H_2SO_4$ mole ratio (54.3); $t$ = 0.51 s

| Organic solvent, M | Wave no. 1 | | | Wave no. 2 | | |
|---|---|---|---|---|---|---|
| | $-I_{lim}$, μA | $-E_{1/2}$, mV | tan β, mV | $-I_{lim}$, μA | $-E_{1/2}$, mV | tan β, mV |
| AcOH | | | | | | |
| 0 | 0.17 | 210–260 | 150–200 | 3.17 | 830 | 140 |
| 1 | 0.21 | 85 | 140 | 3.10 | 865 | 130 |
| 3 | 0.35 | 55 | 130 | 2.77 | 880 | 115 |
| 5 | 0.38 | 50 | 120 | 2.30 | 880 | 115 |
| 8 | 0.56 | 60 | 110 | 1.62 | 865 | 115 |
| MeCN | | | | | | |
| 1.1 | 0.32 | 95 | 150 | 3.04 | 915 | 120 |
| 3.3[a] | 0.40 | 70 | 125 | – | | |
| 5.5 | 0.51 | 40 | 110 | – | | |
| 8.8 | 0.59 | 15 | 85 | – | | |

[a] Wave no. 2 is overlapped by the wave of reduction of hydroxonium ions. This wave disappears completely at the acetonitrile concentration 5.5 M, despite the fact that in the solution containing 8.8 M MeCN current $I'_{a2}$ is still registered.

that is best expressed at the 3 M $H_2SO_4$ concentration (Fig. 8) and the second wave almost disappear at 5 M $H_2SO_4$ concentration. At further increase in the content of $H_2SO_4$ in the solution the electron transfer onto Ti(IV) is facilitated and in 7 M sulfuric acid becomes reversible (Table 5).

Increase in $H_2SO_4$ concentration is reflected also by the morphology of commutated voltammograms. In particular, decrease in $H_2O/H_2SO_4$ mole ratio leads to a

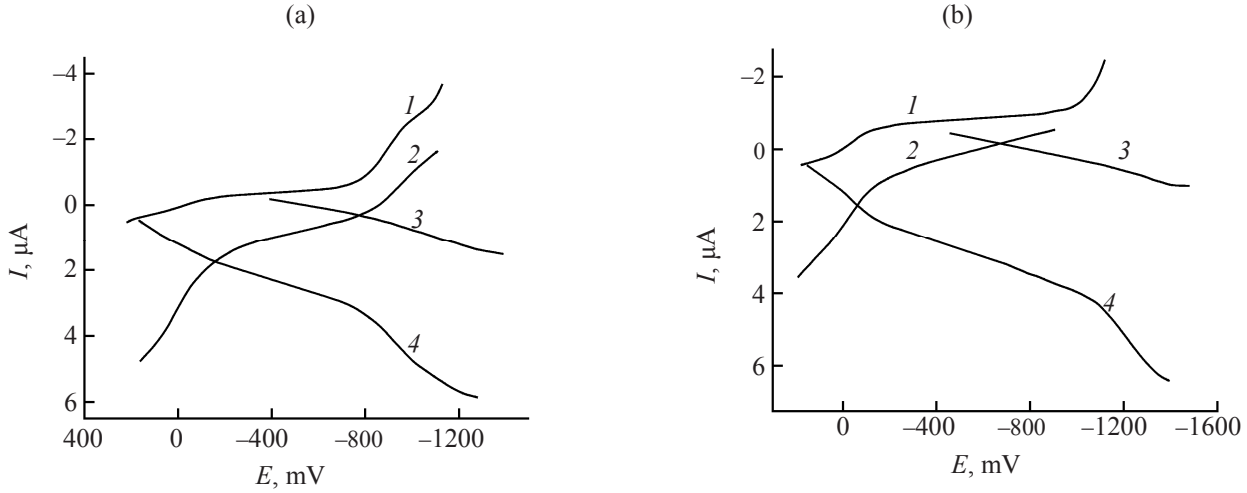


**Fig. 7.** (*1*) Classical and commutated by (*2*) Ist and (*3, 4*) IInd schemes polarograms of Ti(IV) solutions containing (a) 5 M AcOH or (b) 5.5 M MeCN; $H_2O/H_2SO_4$ mole ratio = 54.3, $t$ = 0.51 s.

**Table 5.** Effect of $H_2SO_4$ concentration on the electrochemical parameters of classical polarogram of Ti(IV) reduction in solutions containing 5 M AcOH. $C_{Ti(IV)}$ = 0.001 M, $t$ = 0.51 s

| $C(H_2SO_4)$, M | Wave no. 1 | | | Wave no. 1 | | |
|---|---|---|---|---|---|---|
| | $-I_{lim}$, μA | $-E_{1/2}$, mV | tan β, mV | $-I_{lim}$, μA | $-E_{1/2}$, mV | tan β, mV |
| 0.1[a] | 0.35 | –35 | 125 | 0.97 | –860 | 115 |
| 1 | 0.32 | –50 | 100 | 2.74 | –890 | 120 |
| 2 | [b] | | | 2.10 | –845 | 125 |
| 3 | [b] | | | 1.75 | –800 | 135 |
| 4 | [b] | | | [c] | | |
| 5 | 1.50 | 40 | 70 | [d] | | |
| 6 | 1.31 | 75 | 65 | [d] | | |
| 7 | 1.10 | 105 | 60 | [d] | | |
| 8 | 0.90 | 140 | 60 | [d] | | |
| 9 | 0.70 | 170 | 60 | [d] | | |

[a] $C_{Ti(IV)} = 2.78\times10^{-4}$ M. [b] The treatment of the wave is hindered because of the presence of a maximum. [c] This wave not reaching the limiting current coincides with the wave of reduction of hydroxonium ions; its height is comparable with the height of the wave no. 1. [d] Wave is absent.

**Table 6.** Electrochemical characteristics of classical polarogram of Ti(IV) reduction in sulfuric acid solutions containing 5.5 M MeCN. $C_{Ti(IV)}$ = 0.001 M, $t$ = 0.51 s

| $C(H_2SO_4)$, M | Wave no. 1[a] | | |
|---|---|---|---|
| | $-I_{lim}$, μA | $-E_{1/2}$, mV | tan β, mV |
| 1 | 0.49 | –50 | 85 |
| 3[b] | | | |
| 4[b] | | | |
| 5[b] | | | |
| 6 | 1.64 | 60 | 65 |
| 7 | 1.46 | 95 | 60 |
| 8 | 1.24 | 125 | 60 |
| 9[c] | ~0.97 | ~155 | 60 |

[a] Wave no. 2 is overlapped by the wave of electrochemical reduction of hydroxonium ions. [b] Treatment of the wave is hindered because of the presence of a maximum. [c] Treatment of the wave is rather rough as a result of the absence of the clearly expressed plateau between the waves of mercury oxidation and Ti(IV) reduction.

decrease in $I_{a2}/I_{a1}$, and the second wave in the polarogram commutated along the II-nd scheme like the wave no. 2 in the classical polarogram is not registered at the polarography of solutions with sulfuric acid concentration above 5 M at the potential of limiting current of Ti(III) oxidation. Efficiency of the cathodic generation of Ti(III) reaches 1 in 7 M $H_2SO_4$. The anomalously high values of $-I_a^{\Sigma}/I_{lim}^{\Sigma}$ ratio observed for the aqueous-organic solutions with 0.1 and 9 M $H_2SO_4$ (1.27 and 1.22 respectively) are probably a consequence of chemical reduction of Ti(IV) ions by metallic mercury [8], because in this range there is no clearly expressed region of the potentials separating the wave of mercury oxidation and the first wave of titanium(IV) reduction. The shift of the wave no. 1 to higher cathodic potentials, diminishing of tan β (Table 5) and appearance of plateau between this wave and the wave of mercury oxidation at the increase in sulfuric acid concentration from 0.1 to 1 M can be caused by the change in ligand

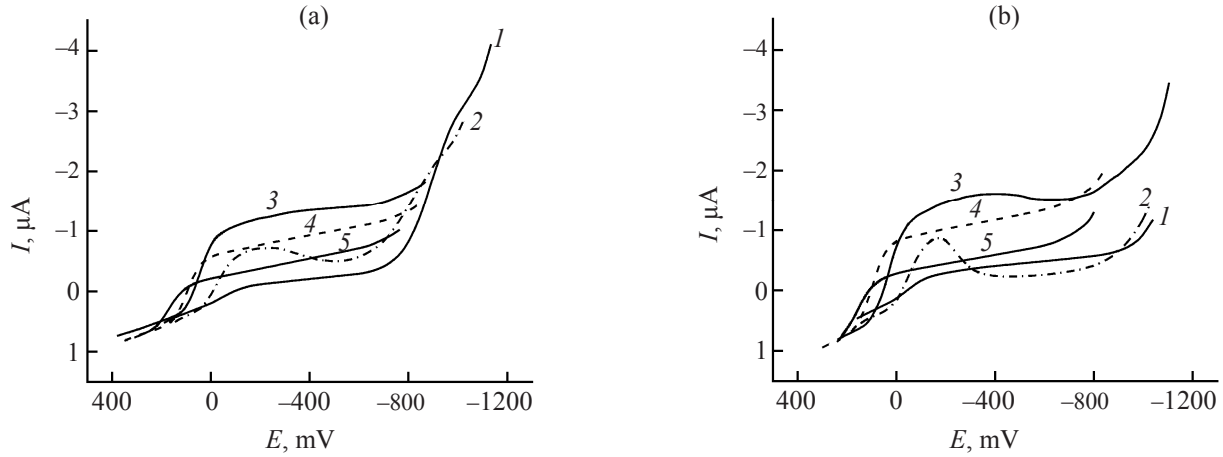


**Fig. 8.** Effect of $H_2SO_4$ concentration on the appearance of classical polarogram of Ti(IV) reduction in solutions containing (a) 5 M AcOH or (b) 5.5 M MeCN. $C(H_2SO_4)$, M: (*1*) 1, (*2*) 3, (*3*) 5, (*4*) 7, and (*5*) 9.

surrounding of Ti(IV). It is possible to suggest that in 1 M $H_2SO_4$ the complex formation proceeds with the involvement of acetic acid molecules mainly while in the less acidic solution acetate ions are also involved.

In the polarograms obtained from the Ti(IV) solutions containing 5.5 M of MeCN (Table 6) the wave no. 2 does not appear at all. Increase in $H_2SO_4$ concentration leads to the appearance of a maximum at the potentials of the first wave, but it is registered in a narrower potential range than the analogous maximum at the polarography of solutions containing acetic acid (Fig. 8) and is seen sufficiently well at 5 M concentration of $H_2SO_4$. In 5 M $H_2SO_4$ the weakly expressed second wave also is still registered in the polarogram commutated along the IInd scheme at the potential of limiting current of Ti(III) oxidation. Moreover, despite the fact that heterogenous electron transfer in 7 M $H_2SO_4$ containing MeCN is reversible, the efficiency of Ti(IV) reduction under these conditions still remains below unity (0.91).

The experiments performed at the constant $H_2O$/$H_2SO_4$ mole ratio corresponding to 9 M $H_2SO_4$ [Table 7; like in the case of 1 M $H_2SO_4$ the increase in the content of organic solvents in the electrolyte decreased the concentration of Ti(IV) ions] showed that in sulfuric acid solutions where a fast exchange occurred between the electrode and titanium ions the effect of AcOH and MeCN on the heterogenous process is not considerable.

Thus, polarographic investigations showed that organic solvents play a dual role in the processes of electrochemical amination of unsaturated and aromatic compound. They not only increase solubility of substrates in the catholyte but also affect the results of addition and substitution via the composition of the complexes of the mediator system Ti(IV)/Ti(III). The degree of this influence diminishes at the increase in $H_2SO_4$ concentration.

## EXPERIMENTAL

Investigations were carried out at 25°C using glass polarographic cell with temperature-controlling jacket. The voltammograms were recorded in three-electrode regime on the polarographs PU-1, RA-2 and two-coordinate recorder LKD4-003. Potential sweep rate was 5 mV $s^{-1}$.

At the registration of classical polarograms of Ti(IV) and Ti(III) and commutated polarograms of Ti(IV) solutions as the operating and auxiliary electrodes were used dropping mercury electrode (DME, besides a specially mentioned case the mercury outflow rate was 3.6 mg $s^{-1}$) and bottom mercury. The DME potential was measured relatively to a silver chloride reference electrode. The required dropping period of DME ($t$) was provided with electromagnetic drop knocker. The commutated polarograms were recorded with Ist and IInd commutation schemes [16] by means of electronic switch, the commutation frequency was 10 Hz.

**Table 7.** Electrochemical characteristics of the polarogram of Ti(IV) reduction in solutions with constant $H_2O$ : $H_2SO_4$ mole ratio (3.75); $t$ = 0.51 s

| Organic solvent, M | $-I_{lim}$, μA | $-E_{1/2}$, mV | tan β, mV |
|---|---|---|---|
| | AcOH | | |
| 0 | 1.63 | 100 | 60 |
| 1 | 1.35 | 100 | |
| 3 | 1.06 | 100 | |
| 5 | 0.84 | 95 | |
| 8 | 0.65 | 95 | |
| | MeCN | | |
| 1.1 | 1.39 | 100 | 60 |
| 3.3 | 1.18 | 95 | |
| 5.5 | 0.97 | 90 | |
| 8.8 | 0.80 | 80 | |

Prior to the registration of voltammograms the oxygen dissolved in working electrolyte was removed by the flow of argon passed through a Drexel bottle with a solution identical to the studied one. In the course of the experiment the argon flow was passed over the electrolyte.

In the work was used mercury purified by standard procedure, 15% solution of titanium(IV) sulfate in 4 M sulfuric acid (analytically pure grade); a solution of Ti(III) prepared from the above mentioned solution by reduction of Ti(IV) in the electrochemical cell with cathode and anode spaces separated by a ceramic diaphragm; sulfuric acid (chemically pure grade); distilled acetic acid (chemically pure grade); acetonitrile (analytically pure grade) treated with $KMnO_4$ and distilled over $P_2O_5$; twice distilled water.

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