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Polarography of Te (IV) Anions in Neutral Solutions in Presence of 2,2'-Dipyridyl and $Fe(dipy)_3^{2+}$-Complexes

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Abstract

The electroreduction of Te (IV) ions in neutral non-buffer solutions containing 2,2'-dipyridyl ($4\cdot10^{-5}$-$4\cdot10^{-3}$ M) or tris-dipyridyl iron (II) complexes is studied by the polarographic method. NaF (0.01-0.5 M) or $NaNO_3$ (0.1-1 M) are used as supporting electrolytes. The mechanism of electrochemical reactions of Te (IV) anions on mercury electrodes in the presence of the additives is discussed. The electroreduction of Te (IV) anions is shown to proceed through electron transfer and proton addition.

The obtained results point to a considerable influence of electric double layer structure on electrochemical reactions of Te (IV) ions in the presence of inorganic and specifically adsorbed organic compounds in the electrolyte. It is shown, that 2,2'-dipyridyl does not form complexes with Te (IV) anions. Having been adsorbed on the surface of mercury electrode, 2,2'-dipyridyl complexes increase negative Ψ'-potential that results in a shift of Te (IV) electroreduction wave to more negative potentials and decrease in the current of Te (IV) wave and peak at -1.19 V. It is shown that 2,2'-dipyridyl molecules at $\varepsilon > 0$, (ε – charge of an electrode) are adsorbed in plane orientation, and at $\varepsilon < 0$, plane or vertical. Vertically adsorbed molecules cause a significant decrease in the double layer capacitance. At negative potentials orientation of 2,2'-dipyridyl molecules changes from plane to vertical with the increasing 2,2'-dipyridyl concentration. This change of orientation results in a typical maximum capacitance emerging in the potential range of -0.7 to -1.2 V.

It is shown that the supporting electrolyte, 2,2'-dipyridyl and $Fe(dipy)_3^{2+}$ have influence on the electroreduction of Te (IV) anions in neutral non-buffer solutions through a change in the Ψ'-potential of mercury electrode.

Introduction

It is known [1-3] that electroreduction of Te (IV) at mercury electrode involves two simultaneous processes occurring in the potential range of 0 to -1.3 V:

$$Te\ (IV) + 6e \rightarrow Te^{2-} \qquad (1)$$

The potential of maximum at E = -1.19 V corresponds to the potential of half-wave $E_{1/2}$ in reaction (2). The summed reduction current can be described by the reaction (3):

$$Te^{2-} - 2e \rightarrow Te^0 \qquad (2)$$

$$Te\ (IV) + 4e \rightarrow Te^0 \qquad (3)$$

Reaction (2) does not proceed at the potentials more negative than the potential of maximum (-1.19 V). The limiting diffusion current corresponds to four electron reduction of Te (IV) due to the reaction (4):

$$Te\ (IV) + 2Te^{2-} = 3Te^0 \qquad (4)$$

However, many questions related to the mechanism of Te (IV) reduction remain unanswered. For example, different authors [4-6] explain in different ways the emergence of peak current at -1.19 V. In [4] this maximum is considered to be polarographic method. In [5] the occurrence of this maximum is accounted for by catalytic liberation of hydrogen on elemental tellurium. The adsorption nature of this maximum and its relation to the redaction of adsorbed Te (0) to telluride ions is shown in [6]. In previous and some current publications little attention has been paid to the form of existence of Te (IV) ions in solution and at the electrode surface. The influence of double electric layer structure on the electrochemical behavior of Te (IV) ions in the presence of inor-

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ganic and specifically adsorbed organic compounds is seldom taken into account.

Recently we found that little additives of 2,2'-dipyridyl improve electrodeposition CdTe thin films [7]. Hence the mechanism of influence of 2,2'-dipyridyl on this process and especially on the electroreduction of Te (IV) is not clear.

This paper deals with the influence of adsorption of 2,2'-dipyridyl (dipy) and $Fe(dipy)_3^{2+}$ complexes on electroreduction of Te (IV) anions. It is assumed that Te (IV) ions are anions in the pH range chosen (7-8) and that electroreduction of Te (IV) at mercury drop electrode proceeds at potentials of maximum adsorption of 2,2'-dipy and $Fe(dipy)_3^{2+}$ complexes.

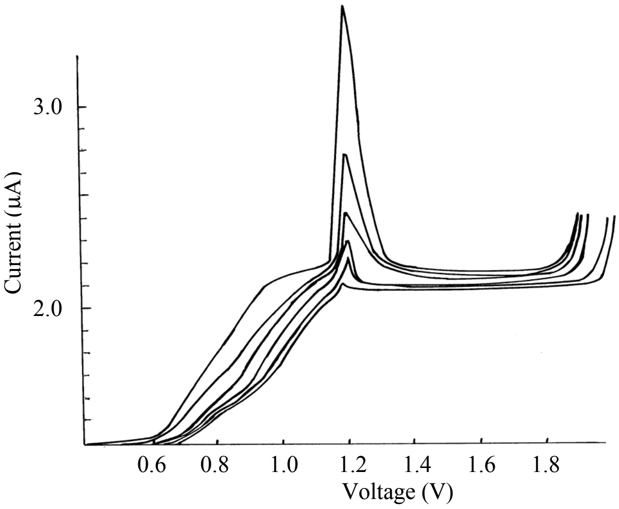
Measurement Procedure

The electroreduction of Te (IV) ions was studied with 2,2'-dipyridyl and $Fe(dipy)_3^{2+}$ complexes by polarographic methods (both classical and alternating current) using PU-1-polarograph. The measurements were carried out in a hermetically sealed three-electrode glass cell in helium medium. Dropping mercury electrode (DME) was used as a working electrode. The rate of mercury flow was m = 1.05 mg/s, and the drop period was t = 4.4 s at H = 97.51 cm mercury column height. The potential of DME was measured relative to chlorine-silver electrode in saturated NaCl solution. The potential of reference electrode was 198 mV with respect to hydrogen electrode. In this work, all the potentials are given with respect to Ag/Cl electrode. $Na_2TeO_3{\cdot}2H_2O$ (Reagent Grade), $Fe(NH_4)_2(SO_4)_2{\cdot}6H_2O$ (Reagent Grade), and 2,2'-dipyridyl produced by Reanal (Hungary) were used as initial reagents. All the salts were recrystallized, and solutions were prepared using twice distilled water. The experiments were conducted at 25±0.2°C temperature in aqueous non-buffer solutions (pH ≈ 7.0). Under these conditions, 2,2'-dipyridyl was present in solutions in the form non-protonated molecules.

Results

Classical polarograms of Te (IV) on DME using NaF (0.5-0.01 M) supporting electrolyte have been obtained to study the effect of electric double layer structure on Te (IV) reduction, and reasons of its change. The wave of Te (IV) reduction has a complicated form (see Fig. 1, curve 1) with two peaks observed on the wave of Te (IV) reduction before limiting current is reached. The first peak at E = -1.03 V potential is plane and the second one at E = -1.19 V potential is sharp. The first peak current is growing proportionally to increase in the mercury column height (H) confirming its adsorption nature. The peak current at -1.19 V, vice versa, decreases with the increasing mercury column height. The peak current for Te (IV) wave displayed at more negative potentials than -1.19 V, is due to the diffusion of Te (IV) ions to the DME surface because $I_{lim}=f(H^{1/2})$. This is consistent with the literature data [1,2].

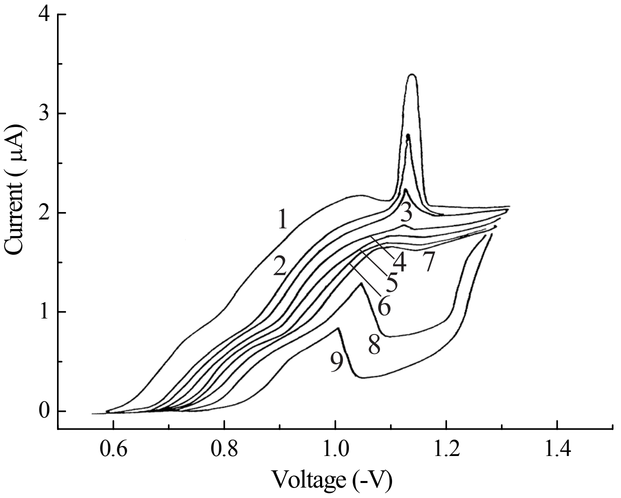
The Te (IV) wave shifts in the direction of more negative potentials with decreasing ionic strength of solution; and emergence of two waves on it can be identified. They are clearly seen when NaF concentration is 0.01 M (Fig. 1, curve 2). The decrease in NaF concentration reduces limiting current for Te (IV) wave and the maximum at E = -1.19 V.



$C_{Te\ (IV)} = 2.7{\cdot}10^{-4}$ M. C_{NaF}: 1 – 0.005 M; 2 – 0.01 M; 3 – 0.05 M; 4 – 0.1 M; 5 – 0.2 M; 6 – 0.5 M.
Fig. 1. Polarograms for Te (IV) electroreduction in the supporting electrolyte NaF.

Above mentioned experimental data point to the influence of electric double layer structure on the electroreduction of Te (IV) on DME. Indeed, the absolute value of negative potential (ψ') decreases with the increase in NaF concentration. This accelerates electrochemical reaction of Te (IV) reduction provided that depolarizer are anions reducing irreversibly.

In Figure 2, we present classical polarograms of Te (IV) electroreduction on DME in 0.1 M NaF solution without 2.2'-dipyridyl (Curve 1) and at varying concentrations of 2,2'-dipyridyl from $4{\cdot}10^{-5}$ to $4.4{\cdot}10^{-3}$ M (curves 2-9).

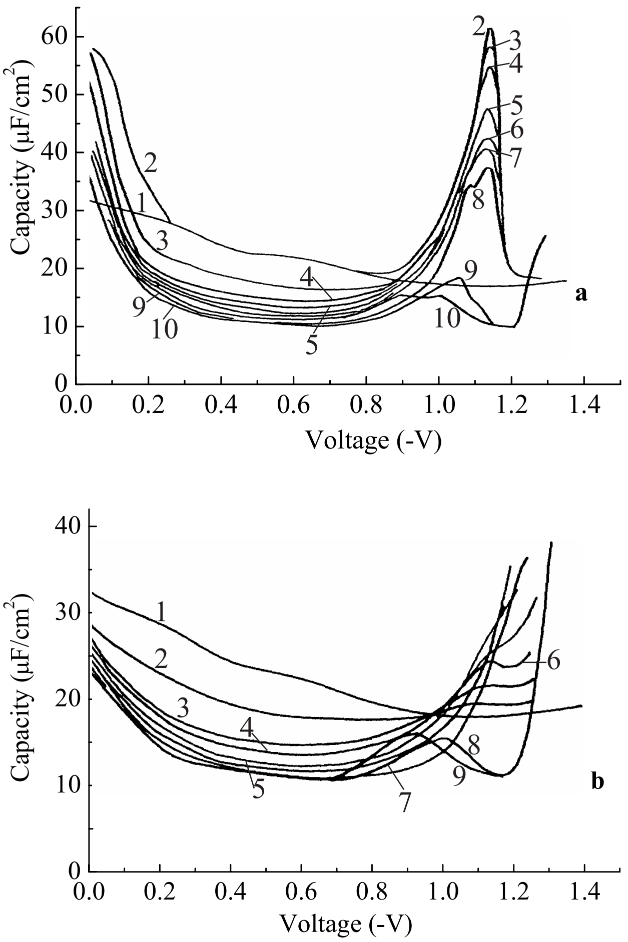


$C_{Te\ (IV)} = 2.0 \cdot 10^{-4}$ M. C_{dipy}: 1 – 0; 2 – $4 \cdot 10^{-5}$; 3 – $1 \cdot 10^{-4}$; 4 – $2 \cdot 10^{-4}$; 5 – $3.8 \cdot 10^{-4}$; 6 – $7.4 \cdot 10^{-4}$; 7 – $1.5 \cdot 10^{-3}$; 8 – $2.8 \cdot 10^{-3}$; 9 – $4.4 \cdot 10^{-3}$.

Fig. 2. Polarograms for Te (IV) electroreduction in the supporting electrolyte 0.1 M NaF.

The incorporation of $4 \cdot 10^{-5}$ M 2,2'-dipyridyl (Fig. 2, curve 2) into the solution results in disappearance of plane peak at -1.03 V, having adsorption nature. The increase in 2,2'-dipyridyl concentration to $7.4 \cdot 10^{-4}$ M shifts the wave of Te (IV) reduction to more negative potentials. The magnitude of shift reaches ≈ 120 mV. The increase in 2,2'-dipyridyl concentration causes also marked split of Te (IV) wave. The peak current at -1.19 V also decreases with an increase in 2,2'-dipyridyl concentration (Fig. 1, curves 2-5). Current decay can be seen at 2,2'-dipyridyl concentration higher than 10^{-3} M, instead of the peak in this range of potentials (Fig. 2, curves 8-9). The decay tends to expand to the range of more positive potentials with the increasing 2,2'-dipyridyl concentration. The value of current decay does not depend on the mercury column height. This current should, probably, be considered as kinetic penetration current when the surface coverage is close to 1 (Loshkarev effect).

The alternating current polarograms of Te (IV) in the presence of 2,2'-dipyridyl have been obtained in the "capacitance" mode to get additional information about processes occurring on DME surface during Te (IV) reduction. Differential capacitance curves for DME in 0.1 M NaF solution at different concentrations of 2,2'-dipyridyl are shown in Fig. 3. It can be seen that 2,2'-dipyridyl significantly reduces peak capacitance at (E_n = -1.19 V), the potential of which coincides with a similar peak current on the polarograms.



a) $C_{Te\ \{IV\}} = 2 \cdot 10^{-4}$; C_{dipy}: 1, 2 – 0; 3 – $4 \cdot 10^{-5}$ M; 5 – $2 \cdot 10^{-4}$ M; 6 – $3.8 \cdot 10^{-4}$ M; 7 – $7.4 \cdot 10^{-4}$ M; 8 – $1.5 \cdot 10^{-3}$ M; 9 – $2.8 \cdot 10^{-3}$ M; 10 – $4.4 \cdot 10^{-3}$ M.

b) C_{dipy}: 1 – 0; 2 – $4 \cdot 10^{-5}$ M; 3 – $1 \cdot 10^{-4}$ M; 4 – $2 \cdot 10^{-4}$ M; 5 – $3.8 \cdot 10^{-4}$ M; 6 – $7.4 \cdot 10^{-4}$ M; 7 – $1.5 \cdot 10^{-3}$ M; 8 – $2.8 \cdot 10^{-3}$ M; 9 – $4.4 \cdot 10^{-3}$ M.

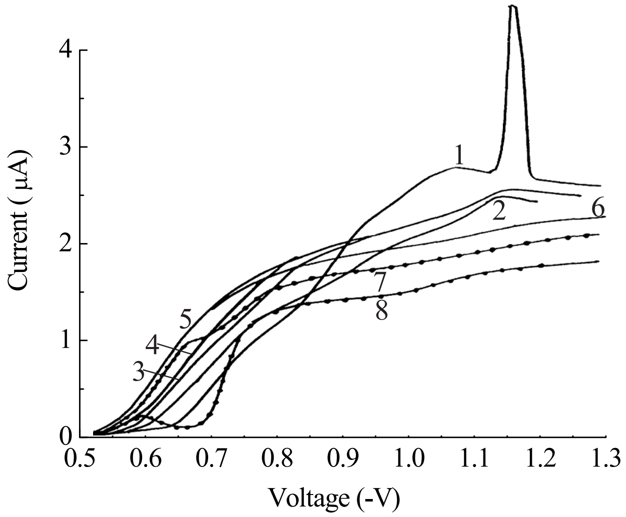
Fig. 3. Dependence of differential capacity of DME on potential.

The comparison of C(*E*)-curves (Fig. 3a) with similar curves in the absence of Te (IV) ions (Fig. 3b) shows that the presence of Te (IV) ions does not affect significantly capacity in -0.2 to -0.6 V range of potentials within which no Faraday current of Te (IV) electroreduction is available.

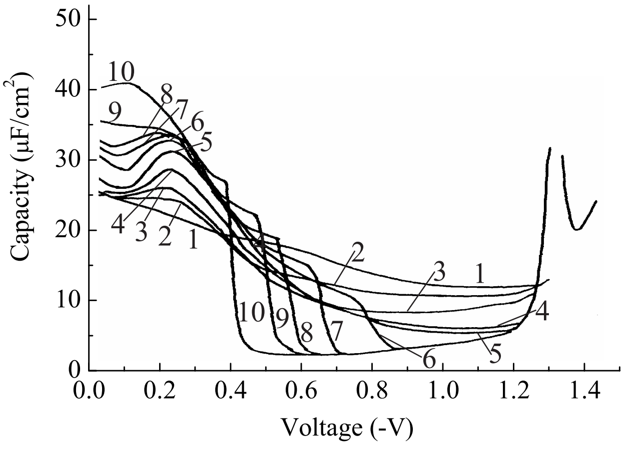
The effect of tris-dipyridyl Fe (II) complexes on electroreduction of Te (IV) is shown in Figs. 4-6. One can see that even low concentration of $Fe(dipy)_3^{2+}$ ($1.3 \cdot 10^{-5}$ M) in the solution eliminates peak at -1.19 V potential and shifts the Te (IV) electroreduction wave to less negative potentials (Fig. 4, curves 2-6). This shift is greater in the lower part of wave reaching ≈ 120 mV. However, further increase in $Fe(dipy)_3^{2+}$ concentration shifts wave of Te (IV) reduction to the region of more negative potentials and reduces limiting current. When the concentration of $Fe(dipy)_3^{2+}$ is more than 10^{-3} M, clear current decay is displayed in the potential range of -0.6 ÷ -0.7 V (Fig. 4, curve 8). This decay is consistent with the decrease in the DME capacity on C(*E*) curves occurring during $Fe(dipy)_3^{2+}$ adsorption in 0.1 M NaF (Fig. 5).

The increase in the drop period from 4.4 to 10 s reduces current decay on polarograms though DME surface coverage by the adsorbed $Fe(dipy)_3^{2+}$ complexes would grow with the increasing drop period.

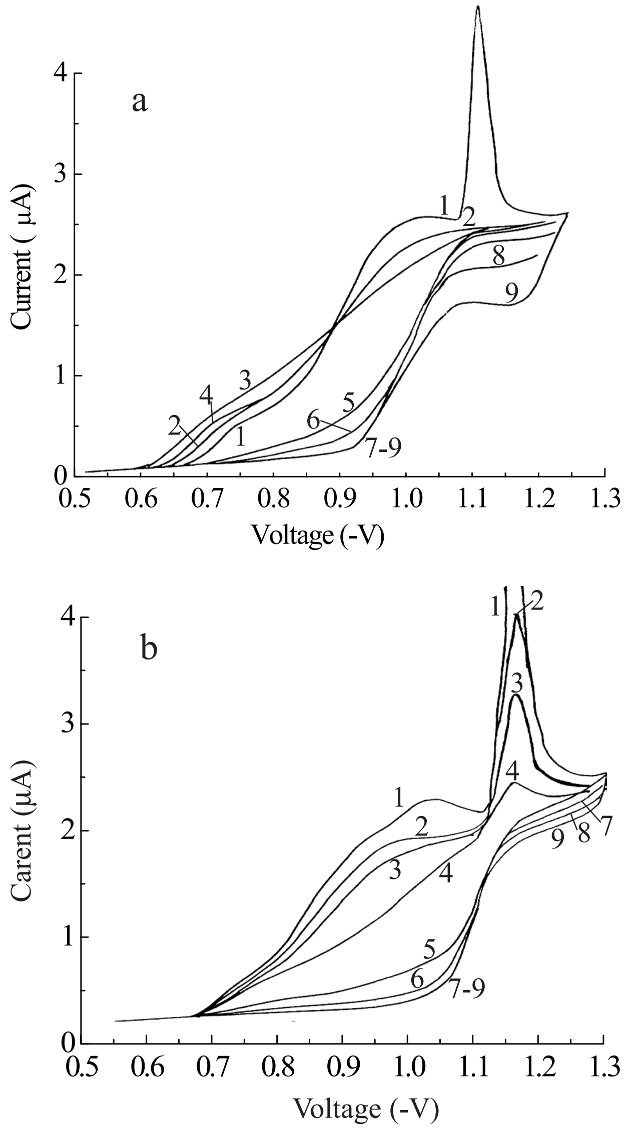
Slight shift of the Te (IV) reduction wave towards less negative potentials is observed when 0.1 M $NaNO_3$ is used as a supporting electrolyte (Fig. 6a, curve 2). The increase in $Fe(dipy)_3^{2+}$ concentration from $1.3\cdot10^{-5}$ M to $3.3\cdot10^{-5}$ shifts the Te (IV) wave in the direction of more negative potentials and reduces the limiting current. The increase in $NaNO_3$ concentration from 0.1 M to 1M also shifts the Te (IV) wave to more negative potentials upon incorporation of $Fe(dipy)_3^{2+}$ complexes (Fig. 6b). The increase in $NaNO_3$ concentration hinders Te (IV) reduction by $Fe(dipy)_3^{2+}$ adsorbed complexes (Fig. 6).



$C_{Te(IV)} = 2.0\cdot10^{-4}$ M at different concentrations $Fe(dipy)_3^{2+}$: 1 – 0; 2 – $3.3\cdot10^{-5}$ M; 3 – $6.7\cdot10^{-5}$ M; 4 – $1.3\cdot10^{-4}$ M; 5 – $2.5\cdot10^{-4}$ M; 6 – $5\cdot10^{-4}$ M; 7 – $9.3\cdot10^{-4}$ M; 8 – $1.5\cdot10^{-3}$ M.
Fig. 4. Polarograms for Te (IV) electroreduction in the supporting electrolyte 0.1 M NaF.



$C_{Fe(dipy)_3^{2+}}$: 1– 0; 2 – $1.3\cdot10^{-5}$ M; 3 – $3.3\cdot10^{-5}$ M; 4 – $6.7\cdot10^{-5}$ M; 5 – $1.3\cdot10^{-4}$ M; 6 – $5.5\cdot10^{-4}$ M; 7 – $1\cdot10^{-3}$ M; 8 – $1.9\cdot10^{-3}$ M; 9 – $2.9\cdot10^{-3}$ M; 10 – $6.6\cdot10^{-3}$ M.
Fig. 5. Dependence of differential capacity of DME on potential.



$C_{Te(IV)} = 2\cdot10^{-4}$ M for different concentrations of $Fe(dipy)_3^{2+}$. $C_{Fe(dipy)_3^{2+}}$: 1 – 0; 2 – $1.3\cdot10^{-5}$ M; 3 – $3.3\cdot10^{-5}$ M; 4 – $6.7\cdot10^{-5}$ M; 5 – $1.3\cdot10^{-4}$ M; 6 – $2.5\cdot10^{-4}$ M; 7 – $5\cdot10^{-4}$ M; 8 – $9.3\cdot10^{-4}$ M; 9 – $1.5\cdot10^{-3}$ M. a – 0.1 M $NaNO_3$; b – 1 M $NaNO_3$.
Fig. 6. Polarogramms for Te (IV) electroreduction.

Discussion

The obtained results point to a considerable influence of electric double layer structure on electrochemical reactions of Te (IV) ions in the presence of inorganic and specifically adsorbed organic compounds in the electrolyte.

The experimental results confirm that negative particles of Te (IV) undergo discharge on the DME, because the wave of Te (IV) electroreduction shifts in the direction of more negative potentials with the decreasing NaF-concentration (Fig. 1). Such particles can be Te (IV) in the form of anions. According to [7], Te (IV) ions can exist as $HTeO_3^-$ and TeO_3^{2-} at pH = 7÷8, and under the present experimental conditions, their concentrations are comparable.

The decrease in NaF concentration from 0.5 to 0.001 M increases absolute value of negative Ψ'-potential, inhibiting discharge of Te (IV) anions. The effect of Ψ'-potential would have been opposite with Te (IV) cations. The decrease in the cathode current peak at -1.19 V can be due to decrease in Te concentration caused by the inhibition of reactions (5-7):

$$TeO_3^{2-} + 3H_2O + 4e \rightarrow Te + 6OH^- \tag{5}$$

$$HTeO_3^- + 2H_2O + 4e \rightarrow Te + 5OH^- \tag{6}$$

$$Te + 2H^+ + 2e \rightarrow H_2Te \tag{7}$$

This effect occurs when the negative value of the Ψ'-potential increases with the decreasing ionic force of supporting electrolyte and when the concentration of Te (IV) anions at the electrode surface decreases.

Similar effects have been observed on incorporation of 2,2'-dipyridyl into the solution. Having been adsorbed on the surface of mercury electrode, 2,2'-dipyridyl increases the negative Ψ'-potential that results in a shift of Te (IV) electroreduction wave to more negative potentials and decreases in the current of Te (IV) wave and peak at -1.19 V. We believe that the shift is not due to formation of Te (IV) complexes with 2,2'-dipyridil since we have failed to find such information in the literature [9].

The change of 2,2'-dipyridyl concentration from $4 \cdot 10^{-5}$ to 10^{-3} M (Fig. 1, curves 2-5) affects the shape of Te (IV) polarograms as does the change of NaF concentration from 0.5 to 0.01. Such similarity, apparently, points to similar nature of Te (IV) interaction with 2,2'-dipyridyl and NaF at the mercury electrode surface.

It is known that 2,2'-dipyridyl molecules at $\varepsilon > 0$, (ε – charge of an electrode) are adsorbed in plane orientation, and at $\varepsilon < 0$, plane or vertical [10,11]. Vertically adsorbed molecules cause a significant decrease in the double layer capacitance. At negative potentials the orientation of 2,2'-dipyridyl molecules changes from plane to vertical with the increasing 2,2'-dipyridyl concentration. This change of orientation results in a typical maximum capacitance emerging in the potential range of -0.7 to -1.2 V (Fig. 3b). This maximum shifts in the direction of more positive potentials with the increase in 2,2'-dipyridyl concentration. The decrease in the capacitance at the potentials more negative than -1.0 V and at the 2,2'-dipyridyl concentration more than 10^{-3} M points to the vertical orientation of adsorbed 2,2'-dipyridyl molecules at the mercury electrode (Fig. 3b). Apparently, the molecules adsorbed in plane orientation do not inhibit significantly the transfer of electrons to Te (IV) ions. Negatively charged electrode surface repels π-electrons of 2,2'-dipyridyl, forcing vertical orientation of its molecules. Nitrogen atoms of 2,2'-dipyridyl directed to the solution acquire additional negative charge due to π-electron shift in the electric field of electrode increasing the negative Ψ'-potential and hindering the Te (IV) reduction. Adsorption of hydrophobic 2,2'-dipyridyl molecules on the surface of mercury electrode may also displace adsorbed water molecules, a source of protons for reactions (5-7).

Sharp decrease in the current (Fig. 2, curves 8, 9) of Te (IV) electroreduction when 2,2'-dipyridyl concentration is more than 10^{-3} M (Fig. 3b) is related to the maximum on the differential capacitance curves at $E > -1.0$ V (Fig. 3b) due to vertical reorientation of 2,2'-dipyridyl molecules.

The magnitude of current does not depend on the mercury column height at these potentials and is determined, obviously, by kinetic difficulty of penetration of Te (IV) anions through the layer of adsorbed molecules.

The adsorption of $Fe(dipy)_3^{2+}$ cations on DME, on the contrary, decreases the absolute value of negative Ψ'-potential and thus speeds up the discharge of Te (IV)-anions. This shifts the Te (IV) electroreduction wave to less negative potentials in 0.1 M solution when the $Fe(dipy)_3^{2+}$ concentration varies from $3.3 \cdot 10^{-5}$ to $2.5 \cdot 10^{-4}$ M (Fig. 4, curves 2-5). $Fe(dipy)_3^{2+}$ complexes do not form outer-sphere associates with F^- anions in NaF solutions [12], and therefore, may be related to organic cations. It is known, that $Fe(dipy)_3^{2+}$ complexes are inert in aqueous solutions and have half-exchange period of $\tau^{1/2} = 5$ hours

[13]. Probably, $Fe(dipy)_3^{2+}$ complexes influence electrochemical reactions involving anions and cations similar to hydrophobic tetraalkilammonium cations.

$Fe(dipy)_3^{2+}$ can form outer-sphere complexes of $[Fe(dipy)_3^{2+}]\cdot(NO_3^-)_i$, ($i = 1, 2$). Te (IV) discharge in $NaNO_3$ as a supporting electrolyte in the presence of $Fe(dipy)_3^{2+}$ (Fig. 6) is inhibited by adsorption of these outer-sphere complexes. The share of neutrally charged $[Fe(dipy)_3^{2+}](NO_3^-)_2$ complexes increases with the increasing $NaNO_3$ concentration from 0.1 to 1 M (Fig. 6b). The mutual arrangement of negatively and positively charged fragments of $[Fe(dipy)_3^{2+}](NO_3^-)_2$ complexes provides their attractive interaction. In this case there occurs multi-layer adsorption of the complexes that hinders electron transfer from mercury electrode to Te (IV) anions. So, electroreduction wave shifts drastically in the direction of more negative potentials. We observed similar effects for the adsorption of $Cd(dipy)_1^{2+}(NO_3^-)_2$ electroneutral complexes on mercury electrode [14,15].

Conclusions

It is shown that the supporting electrolyte, 2,2'-dipyridyl and $Fe(dipy)_3^{2+}$ influences the electroreduction of Te (IV) in neutral non-buffer solutions through a change in the Ψ'-potential of mercury electrode. The obtained results confirm that under such conditions only $HTeO_3^-$ and TeO_3^{2-} anions undergo electroreduction. The increase in the negative Ψ'-potential and the decrease in the desorbed water (proton source) amount inhibit the process and eliminate the peak current related to subsequent reduction of Te^0 to Te^{2-}. The adsorption of neutral associates of $Fe(dipy)_3^{2+}$ $(NO_3^-)_2$ increases with growing concentration of nitrate-ion and inhibits the discharge of tellurium (IV). The effect of low ($< 7\cdot10^{-4}$ M) and high ($> 10^{-3}$ M) concentrations of 2,2'-dipyridyl and $Fe(dipy)_3^{2+}$ on the electroreduction of tellurium anions is found to be different.

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