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POLAROGRAPHY OF TECHNETIUM IN PERCHLORATE SOLUTIONS

During the isolation of weighable amounts of technetium from neutron-irradiated molybdenum, it became necessary to find methods for the analysis of technetium and molybdenum in which these two elements would not interfere with one another in the determination. For this reason we undertook a study of the electrochemical properties of technetium by the polarographic method using a dropping mercury electrode. The investigations were carried out against a background of $1\,M$ $NaClO_4$ over a wide range of alkalinity and acidity of the solution. We were interested in whether, in this medium, coupled reactions occur whose result is various kinds of catalytic effects (the catalytic action of an oxidant on the product of electrolytic reduction, catalytic hydrogen evolution), leading to an increase in the sensitivity of the method.

A number of authors have studied polarographic catalytic currents arising from the action of various oxidants on the product of electroreduction of molybdenum ([1,2]), and in particular catalytic waves in hydrochloric acid solutions ([3–5]). Analogous investigations with TcO_4^- have not been described in the literature. There are only indications of studies of the electrochemical properties of this anion in $4\,M$ $HClO_4$ ([6,7]), and it was established that in this solution TcO_4^- gives no distinct electroreduction waves.

In our studies we used chemically and radiochemically pure salts of ammonium pertechnetate. The final purification of NH_4TcO_4 and its identification are described in the article ([8]). The technetium concentration was measured by absolute activity using 4π-geometry*. The reagents used as indifferent background electrolytes were chemically pure. Polarograms were recorded with an electronic polarograph PE-312. The cell held 1–3 ml of solution. The anodic compartment in the cell was separated from the cathodic compartment by a porous glass filter. It was established that diffusion of electrolytes from one compartment of the cell to the other proceeds very slowly under the experimental conditions. Nevertheless, most experiments were performed with one and the same indifferent electrolyte in both compartments of the cell, with 0.01% gelatin added to the

Fig. 1. Polarogram of TcO4— in neutral solutions.

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cathodic compartment. Oxygen was removed from the solution by purging with purified nitrogen. The experiments were carried out at room temperature, 25-26° C. All potentials in the article are referred to the normal calomel electrode. Polarograms were recorded from 0.0 to 2.0 V.

In neutral solutions against a background of 1 M $NaClO_4$, a distinct diffusion wave of TcO_4^- is observed with a half-wave potential $\varphi_{1/2} \sim 0.8$ V (Fig. 1a, curves 2-6). The magnitude of the limiting current of this wave is proportional to the technetium concentration at least in the studied range $0.5 \cdot 10^{-5}$-$8 \cdot 10^{-5}$ M (Fig. 2).

The conclusion that the limiting current of the TcO_4^- wave in neutral solution is diffusive in nature is based on its linear dependence on the height of the mercury column (H) to the power 1/2. The number of electrons entering into the reaction was calculated by the Ilkovič equation:

$$n = \frac{i_{\text{pr}}}{605 C D^{1/2} m^{2/3} t^{1/6}}, \tag{1}$$

* The authors express their gratitude to Prof. S. A. Baranov for measuring the technetium standard preparations.

where i_{lim} is the limiting current, equal to 1 μA; C is the technetium concentration, $8.05 \cdot 10^{-5}$ M; D is the diffusion coefficient of TcO_4^- ions, taken from work (7), equal to $1.56 \cdot 10^{-5}$ cm^2/sec; m is the rate of mercury outflow from the capillary, corresponding to 1.85 mg/sec; τ is the period of mercury dropping from the capillary, 1.85 sec. Substitution of all the indicated values into formula (1) gives $n = 3.4$.

Fig. 1. Polarogram of TcO_4^- in neutral solutions. a—composition of solutions: 1—1M $NaClO_4$ (background); concentration of NH_4TcO_4: 2—$0.52 \cdot 10^{-5}$; 3—$1.11 \cdot 10^{-5}$; 4—$1.64 \cdot 10^{-5}$; 5—$2.2 \cdot 10^{-5}$; 6—$8.05 \cdot 10^{-5}$ M. b—composition of solutions: 1—1M $NaClO_4$ (background); 6—1M $NaClO_4$ $+8.05 \cdot 10^{-5}$ M NH_4TcO_4. $t = 25 \div 26°$, $H = 50$ cm Hg.

The result obtained concerning the occurrence of a three-electron reduction process of TcO_4^- in a neutral solution is in agreement with work (7), whose authors came to the same conclusion in studying the reduction of TcO_4^- on backgrounds of 0.1 M KCl, 0.1 M NH_4Cl, and also with our data for 1M Na_2SO_4 (unpublished), 1M KCl, and 1M KNO_3. The half-wave potential in all cases is ~ -0.8 V, i.e., it is practically independent of the nature of the indifferent electrolyte.

In addition to the purely diffusion wave, two large maxima are observed on the

Fig. 2. Dependence of the limiting-current magnitude on the concentration of technetium in NH4TcO4 solution.

Figure 2: Fig. 2. Dependence of the limiting-current magnitude on the concentration of technetium in NH4TcO4 solution.

Fig. 3. Polarograms of TcO_4^- in acidic solutions.

Figure 3: Fig. 3. Polarograms of TcO_4^- in acidic solutions.

polarogram of a neutral $1M$ $NaClO_4$ solution at $\varphi_{1/2} = -1.4$ and $\varphi_{1/2} = -1.8$ V (Fig. 1b, 6). With an increase in the height of the mercury column, the maxima increase faster than occurs when the current is of a diffusion nature. In addition, a nonlinear dependence of i_{lim} on C is observed. The limiting current at the minimum has a diffusion character.

Fig. 2. Dependence of the magnitude of the limiting current on the technetium concentration in an NH_4TcO_4 solution

When the solution is acidified, a new wave with $\varphi'_{1/2} = -0.6$ V appears on the polarogram. This wave increases with increasing acidity of the solution and then shifts toward less negative potentials (Fig. 3, 2–6). In $4M$ $HClO_4$ no clearly expressed waves are present. In this medium, technetium is reduced by metallic mercury and, in essence, the wave of mercury ions is recorded on the polarogram (Fig. 3, 6).

In alkaline solutions the electroreduction of TcO_4^- has a different character. With gradual alkalization of the initial neutral solution (Fig. 4a, b, 2–6), already at an alkali concentration of $6.3 \cdot 10^{-3}$ M KOH (Fig. 4b, 4) the process becomes two-electron, since according to the Ilkovič equation $n = 2.4$ at $\varphi_{1/2} = -0.87$ V. At an alkali concentration of $0.3N$, a rather distinct separation of the wave occurs (Fig. 4b, 7) at $\varphi_{1/2} = -1.2$.

It should be noted that the polarographic behavior of the pertechnetate ion in perchlorate and sulfate media is almost analogous. It follows from this that

in these solutions the same reduction processes of TcO_4^- take place, namely, in neutral media TcO_4^- is reduced to the tetravalent state; in acidic solutions undissociated molecules of pertechnetic acid $HTcO_4$, formed by rapid recombination of H^+ and TcO_4^- ions, undergo three-electron reduction; finally, in alkaline solutions reduction proceeds to the pentavalent state, and at more negative potentials to the hexavalent state.

Fig. 3. Polarograms of TcO_4^- in acidic solutions. Composition of solutions: 1–1 M $NaClO_4$ (background); 2–1 M $NaClO_4 + 8.05 \cdot 10^{-5}$ M NH_4TcO_4. $HClO_4$ concentration: 3–$1 \cdot 10^{-2}$; 4–$1 \cdot 10^{-1}$; 5–1; 6–4 M. $t = 25 \div 26°$, $H = 50$ cm Hg.

Fig. 4. Polarograms of TcO_4^- in alkaline solutions. a—composition of solutions:

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Figure 4: Fig. 4. Polarograms of TcO_4^- in alkaline solutions.

1—1 M $NaClO_4$ (background); 2—1 M $NaClO_4 + 8.05 \cdot 10^{-5}$ M NH_4TcO_4; KOH concentration: 3—$3.16 \cdot 10^{-3}$; 4—$6.30 \cdot 10^{-3}$; 5—$2.62 \cdot 10^{-2}$; 6—$3.08 \cdot 10^{-2}$ M. b —composition of solutions: 1—1 M $NaClO_4$ (background); 2—1 M $NaClO_4 +$ $8.05 \cdot 10^{-5}$ M NH_4TcO_4; KOH concentration: 3—$3.16 \cdot 10^{-3}$; 4—$6.30 \cdot 10^{-3}$; 5—$2.62 \cdot 10^{-2}$; 6—$3.08 \cdot 10^{-2}$; 7—$2.99 \cdot 10^{-1}$ M. $t = 25 \div 26°$, $H = 50$ cm Hg.

An interesting region of the polarogram of pertechnetate is the waves with maxima. The limiting currents of these waves and the heights of the maxima considerably exceed the value corresponding even to an eight-electron process. These waves with maxima shift into the region of more negative potentials and increase strongly both upon acidification and upon alkalinization.

···of deaeration of the solution. The appearance of the catalytic waves of TcO_4^- and their behavior are practically independent of the nature of the acid, in contrast to MoO_4^{2-}, which gives a catalytic wave in $HClO_4$ and HNO_3.

Analogous waves have also been observed for rhenium (9,10). Their appearance is attributed by the authors to the formation of the rhenide ion Re^-. It seems more probable to us that these waves correspond to the catalytic evolution of hydrogen as a result of a decrease in its overvoltage by metallic technetium. For the analytical chemistry of technetium, an important circumstance is that the catalytic waves of technetium and molybdenum in perchloric-acid solutions are observed at different potentials. This opens a route to the determination of ultramicroquantities of molybdenum in technetium preparations.

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Note: Figure translations are in progress. See original paper for figures.