

POLAROGRAPHY OF TECHNETIUM IN PERCHLORATE SOLUTIONS

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In the isolation of weighable amounts of technetium from neutron-irradiated molybdenum, a need arose for methods of determining technetium and molybdenum in which these two elements did not interfere with each other. For this reason, we studied the electrochemical properties of technetium by polarography with a dropping mercury electrode. The investigation was carried out with 1 M NaClO₄ as the base electrolyte over a wide range of alkalinities and acidities. We were interested in conjugated reactions in the given medium, which would result in a distinct type of catalytic effect (catalytic action of the oxidant on the electroreduction product and the catalytic liberation of hydrogen), leading to an increase in the sensitivity of the method.

A number of authors have studied the polarographic catalytic currents from the action of various oxidants on the electroreduction product of molybdenum [1,2] and in particular, the catalytic waves in perchloric acid solutions [3-5]. No such investigations with TcO₄⁻ have been described in the literature. There is only a report on the electrochemical properties of this anion in 4 M HClO₄ [6,7] and it was established that TcO₄⁻ does not give sharp electroreduction waves in this solution.

In the investigations we used chemically and radiochemically pure salts of ammonium pertechnetate. The final purification of NH₄TcO₄ and its identification have been described [8]. The technetium concentration was measured by means of the absolute activity using 4π-geometry.* The reagents used as indifferent electrolytes were chemically pure. The polarograms were recorded with a PE-312 electronic polarograph. The cell held 1-3 ml of solution. The anode space of the cell was separated from the cathode space by a porous glass filter. It was established that the diffusion of electrolytes from one compartment of the cell into the other was very slow under the experimental conditions. Nonetheless, most of the experiments were carried out with the same indifferent electrolyte in both compartments of the cell with 0.01% of gelatin added to the cathode compartment. Oxygen was removed from the solution by flushing with purified nitrogen. The experiments were carried out at room temperature (25-26° C). All the potentials given in the article are relative to a normal calomel electrode. The polarograms were plotted from 0.0 to 2.0 V.

In neutral solution with 1 M NaClO₄ as the base electrolyte, a sharp diffusion wave of TcO₄⁻ was observed with a half-wave potential $\varphi_{1/2} \sim 0.8$ V (Fig. 1a, curves 2-6). The limiting current of this wave was proportional to the technetium concentration at least over the range studied, i.e., $0.5 \cdot 10^{-5}$ - $8 \cdot 10^{-5}$ M (Fig. 2).

The linear relation of the limiting current of the TcO₄⁻ wave in neutral solution to the height of the mercury column (H) to the power $1/2$ indicated that it was a diffusion current. The number of electrons involved in the reaction was calculated from the Ilkovic equation:

$$n = \frac{i_{\text{lim}}}{605CD^{1/2}\bar{m}^{2/3}\tau^{1/6}}, \quad (1)$$

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 TcO₄⁻ ions, taken from [7] and equal to $1.56 \cdot 10^{-5}$ cm²/sec; $\bar{m}$ is the rate of flow of mercury from the capillary, equal to 1.85 mg/sec; and τ is the dropping period of mercury from the capillary, 1.85 sec. Substituting all these values in formula (1) gives $n=3.4$.

The conclusion that the reduction of TcO₄⁻ in neutral solution is a three-electron process agrees with the work [7], whose authors came to the same conclusion on investigating the reduction of TcO₄⁻ in the base electrolytes 0.1 M KCl and 0.1 M NH₄Cl and also with our data for 1 M Na₂SO₄ (unpublished), 1 M KCl, and 1 M KNO₃. The half-wave potential in all these cases was ~ -0.8 V, i.e., practically independent of the nature of the base electrolyte.

* The authors would like to thank Prof. S. A. Baranov for measuring standard samples of technetium.

In addition to the purely diffusion wave, the polarogram of a neutral solution of 1 M NaClO₄ showed two large maxima with $\varphi_{1/2} = -1.4$ and $\varphi_{1/2} = -1.8$ V (Fig. 1b, 6). With an increase in the height of the mercury column, the maxima increased more rapidly than would have been the case with a diffusion limiting current at the minimum had a diffusion character.

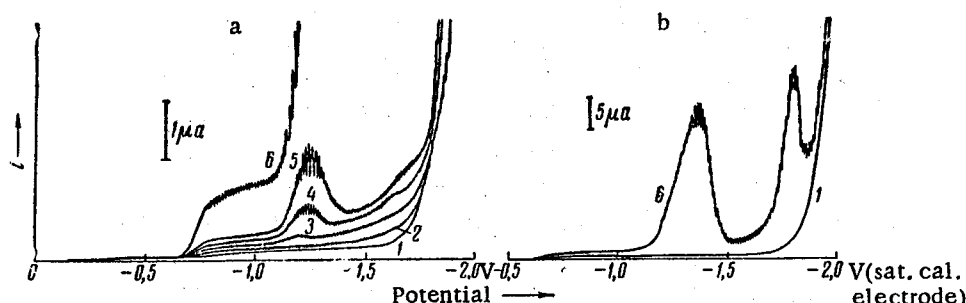


Fig. 1. Polarogram of TcO₄⁻ in neutral solution. a) Solution composition: 1) 1 M NaClO₄ (base electrolyte); NH₄TcO₄ concentration: 2) 0.52·10⁻⁵; 3) 1.11·10⁻⁵; 4) 1.64·10⁻⁵; 5) 2.2·10⁻⁵; 6) 8.05·10⁻⁵ M. b) Solution composition: 1) 1 M NaClO₄ (base electrolyte); 6) 1 M NaClO₄ + 8.05·10⁻⁵ M NH₄TcO₄. t = 25 – 26°, H = 50 cm Hg.

On acidification of the solution, there appeared on the polarogram a new wave with $\varphi_{1/2} = 0.6$ V. This wave increased with an increase in the acidity of the solution and then moved toward less negative potentials (Fig. 3, 2-6). In 4 M HClO₄, there were no sharply expressed waves. In this medium, technetium is reduced by metallic mercury and the polarogram essentially showed the wave of mercury ions (Fig. 3, 6).

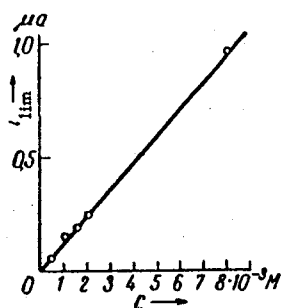


Fig. 2. Relation of limiting current to technetium concentration in NH₄TcO₄ solution.

In alkaline solution, the electroreduction of TcO₄⁻ has a different character. With a gradual increase in the alkalinity of the starting neutral solution (Fig. 4a, b, 2-6), even at an alkali concentration of 6.3 · 10⁻³ M KOH (Fig. 4b, 4), the reduction became a two-electron process, as according to the Ilkovic equation, n = 2.4 at $\varphi_{1/2} = 0.87$ V. At an alkali concentration of 0.3 N there began quite sharp splitting of the wave (Fig. 4b, 7) at $\varphi_{1/2} = -1.2$.

It should be noted that the polarographic behavior of the pertechnetate ion is almost analogous in perchlorate and sulfate media. Hence it follows that the same TcO₄⁻ reduction processes occur in these solutions, namely, in neutral media the TcO₄⁻ is reduced to the tetravalent state, in acid solutions there is three-electron reduction of undissociated molecules of pertechnic acid HTcO₄, formed by rapid recombination of H⁺ and TcO₄⁻ ions, and finally, in alkaline solutions the reduction proceeds to the pentavalent state and at more negative potentials to the hexavalent state.

The interesting region of the pertechnetate polarogram is that with waves having maxima. The limiting currents of these waves and the heights of the maxima considerably exceed the value corresponding to even an eight-electron process. These waves with maxima are displaced toward more negative potentials and increase strongly when the solution is made acid or alkaline. The appearance of TcO₄⁻ catalytic waves and their behavior is practically independent of the nature of the solution, in contrast to MoO₄²⁻, which gives a catalytic wave in HClO₄ and HNO₃.

Analogous waves are observed with rhenium [9, 10]. The authors associated their appearance with the formation of the rhenide ion Re⁻. It seems probable to us that these waves correspond to the catalytic liberation of hydrogen because of the reduction in its overvoltage by metallic technetium. For the analytical chemistry of technetium,

it is very important that the catalytic waves of technetium and molybdenum in perchloric acid solutions appear at different potentials. This offers a method of determining ultramicroamounts of molybdenum in technetium preparations.

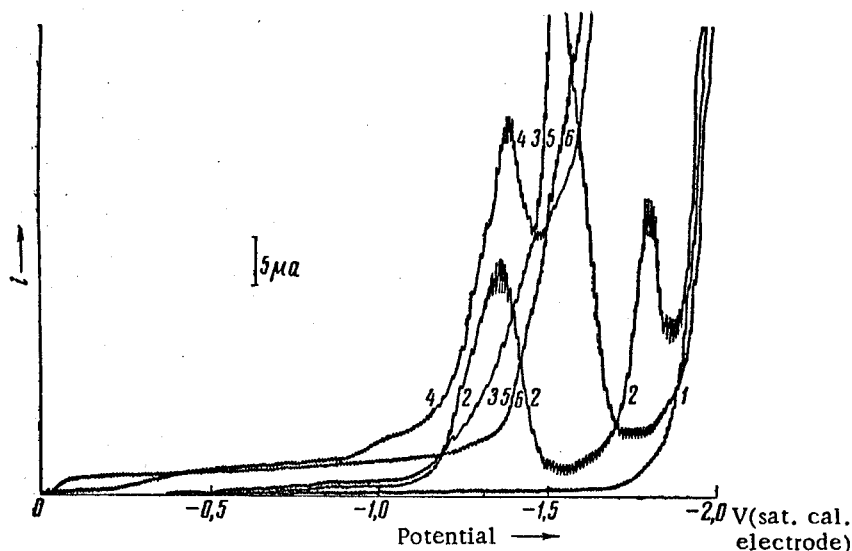


Fig. 3. Polarograms of TcO_4^- in acid solutions. Solution composition: 1) 1 M NaClO_4 (base electrolyte); 2) 1 M $\text{NaClO}_4 + 8.05 \cdot 10^{-5}$ M NH_4TcO_4 ; HClO_4 concentration: 3) $1 \cdot 10^{-2}$; 4) $1 \cdot 10^{-1}$; 5) 1; 6) 4M. $t = 25 - 26^\circ$, $H = 50$ cm Hg.

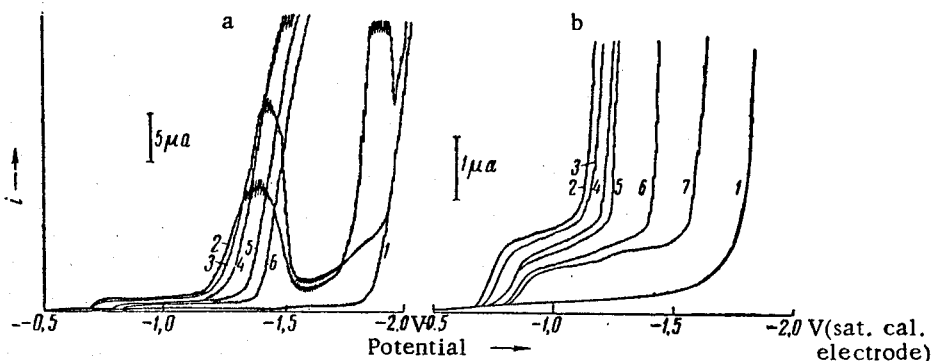


Fig. 4. Polarograms of TcO_4^- in alkaline solutions. a) Solution composition: 1) 1 M NaClO_4 (base electrolyte); 2) 1 M $\text{NaClO}_4 + 8.05 \cdot 10^{-5}$ M NH_4TcO_4 ; KOH concentration: 3) $3.16 \cdot 10^{-3}$; 4) $6.30 \cdot 10^{-3}$; 5) $2.62 \cdot 10^{-2}$; 6) $3.08 \cdot 10^{-2}$ M. b) Solution composition: 1) 1 M NaClO_4 (base electrolyte); 2) 1 M $\text{NaClO}_4 + 8.05 \cdot 10^{-2}$ 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. $t = 25 - 26^\circ$, $H = 50$ cm Hg.

LITERATURE CITED

1. K. B. Yatsimirskii, L. P. Afanas'eva, *ZhAKh*, **11**, 319 (1956).
2. M. C. Johnson, R. J. Robinson, *Anal. Chem.*, **24**, 366 (1952).
3. G. P. Haight, *Anal. Chem.*, **23**, 1505 (1951);
4. G. B. Jones, *Anal. chim. acta*, **10**, 584 (1954).
5. S. I. Sinyakova, M. I. Glinkina, *ZhAKh*, **11**, 544 (1956).

6. R. Colton, J. Dalziel et al., *Nature*, 183, 1755 (1959); *J. Chem. Soc.*, 1960, 71.
7. H. H. Miller, M. T. Kelly, P. F. Thomason, *Advances in Polarography*, Proceedings of the Second Intern. Congr., London, 2, 716 (1960).
8. A. F. Kuzina, *ZhAKh*, 17, No. 4 (1962).
9. J. J. Lingane, *J. Am. chem. Soc.*, 64, 1001, 2182 (1942).
10. R. Geyer, *Zs. anorg. u. allgem. Chem.*, 263, 47 (1950).

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