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Voltammetric Behaviour of Aqueous Technetate(VII) Ion

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The electrochemical behaviour of aqueous TcO_4^- solutions has been studied by cyclic voltammetry in the pH range $-0.5 \div 14$. The reduction products have been identified as TcO_2 and Tc_2O_3. It has been established that the reduction of TcO_4^- occurs, on platinum electrodes, through a chemical step involving adsorbed hydrogen atoms. The oxidation of Tc_2O_3 and TcO_2 to TcO_4^- has been studied, and suggestions for the anodic mechanisms are advanced. The use of the obtained data for analytical procedures and inorganic preparations is suggested.

Introduction

The polarographic behaviour exhibited by technetium in aqueous media has been extensively studied on a large pH range.[1–15] The conclusions drawn by the various authors are however rather different and sometime in evident disagreement. In this connection should be considered the rapidity of the chemical reduction of acidic technetate(VII) by mercury.[7]

At the present no systematic voltammetric study of technetate(VII) ion in non aqueous solvents and on solid electrodes has been reported.

Large scale electrolyses carried out on copper, nickel or platinum electrodes seem to lead to partial deposition of technetium metal with some separation of technetium oxides.[16–19]

The present report deals with the voltammetric behaviour of aqueous solutions of technetate(VII) ion on stationary platinum electrodes in the formal pH range $-0.5 \div 14$. In this investigation, cyclic voltammetry and controlled potential electrolysis have been mainly employed.

Experimental

Chemicals and Reagents

Stock solutions of ammonium technetate(VII) were obtained by dissolving in twice distilled water the recristallized commercial product (Radiochemical Centre Ltd., Amersham, England) according to its formula

TABLE I. Experimental Voltammetric Data.

Solvent	pH	$(Ep)_c$/mV	$(Ep)_{a1}$/mV	$(Ep)_{a2}$/mV	$(Ep)_{a3}$/mV
H_2SO_4 3*M*	–0.5	–110	+580	+700	
H_2SO_4 1*M*	0	–150	+530	+620	
$HClO_4$ 1*M*	0	–120	+540	+620	
HCl 1*M*	0	–170	+550	+630	
HCl 0.1*M*	1	–200	+470	+560	
HCl–NaHcitrate	2	–300	+430	+470	
HCl–NaHcitrate	3	–350	+390		
HCl–NaHcitrate	4	–410	+320		
Citric acid–NaOH	5	–430	+250		
NaH_2PO_4–Na_2HPO_4	7	–560	+110		
HCl–Borax	8	–620	+ 30		
H_3BO_3–NaOH	9	–670	– 30		
H_3BO_3–NaOH	10	–710	–120		
Na_2HPO_4–NaOH	11	–770	–200		
Na_2HPO_4–NaOH	12	–840	–260	–220	–190
NaOH 0.1*M*	13	–880	–320	–270	–230
NaOH 1*M*	14	–930	–390	–330	–270

weight. The purity of the stock solutions was checked by UV spectrophotometry.[20] All others chemicals were reagent grade products and 99,99% nitrogen was employed to remove oxygen from the test solutions.

The buffer solutions (Table I) were used both to obtain the desired pH values and as supporting electrolytes.

Apparatus

The experiments were carried out in H shaped cells, with cathodic and anodic compartments separated by sintered glass disks, at the temperature of 20° C.

The reference electrode was an aqueous SCE; the connections were made by appropriate salt bridges; the counter-electrode was a large mercury pool.

The electrical apparatus employed in the cyclic voltammetric experiments, was a polarographic polarizing unit built up by us with solid state operational amplifier, following a scheme similar to that previously described.[21]

The speed of the potential linear scan could be changed in the range 10–1000 mV s^{-1}.

An Hewlett–Packard XY 7045 A was used to record the voltammetric curves.

An AMEL (Italy) model 557 potentiostat was employed in large scale controlled potential electrolyses. In the voltammetric experiments the working electrode was a spherical platinum microelectrode, while in the macro-electrolyses the polarized electrode was a large platinum foil with an apparent area of 80 square centimeters.

The UV–visible measurements were performed by an Optica CF4 spectrophotometer.

The investigated technetate(VII) concentration ranged between 2×10^{-4} and $2 \times 10^{-3} M$.

Results

Figures 1, 2 and 3 show three typical cyclic voltammetric curves of technetate(VII) ion in three different buffer solutions, at pH values of 18 and 14 respectively.

In acidic media a poorly defined reduction peak at potential values corresponding to the reduction of hydrogen ions to adsorbed hydrogen[22] is exhibited (Figure 1). Associated to the reduction process, two anodic peaks are found only in the presence of TcO_4^- ions, the first one always appears as a shoulder of the larger second anodic peak.

The relative heights of these two peaks do not depend on the potential scan rate, but the first peak increases on increasing the time spent in the reduction process.

In the pH range 3–11, again one cathodic peak is found at potential values corresponding to the reduction of hydrogen ions, but only one anodic process is shown (Figure 2).

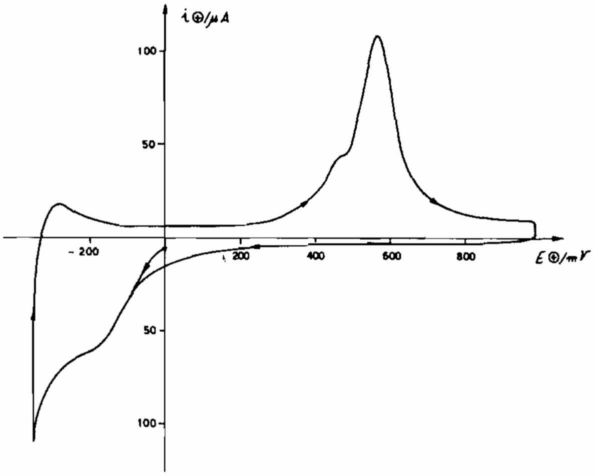


Figure 1. Cyclic voltammetric curve with platinum electrode for a $1 \times 10^{-3} M$ NH_4TcO_4, $0.1 M$ HCl solution; scan rate 100 mV s^{-1}.

In strong alkaline media (pH 12–14) the cathodic process takes place always over the hydrogen ions reduction, while the anodic processes are three (Figure 3). The ratios of the heights of the three anodic peaks markedly depend on the potential scan rate. At a scan rate of 20 mV s^{-1} the first peak, is the highest one, while the third almost disappears; at higher scan rate (1 V s^{-1}) the picture is reversed, namely the first and the second peak are markedly lowered, while the third one is predominant.

The behaviour of the second peak is intermediate between those exhibited by the first and the third

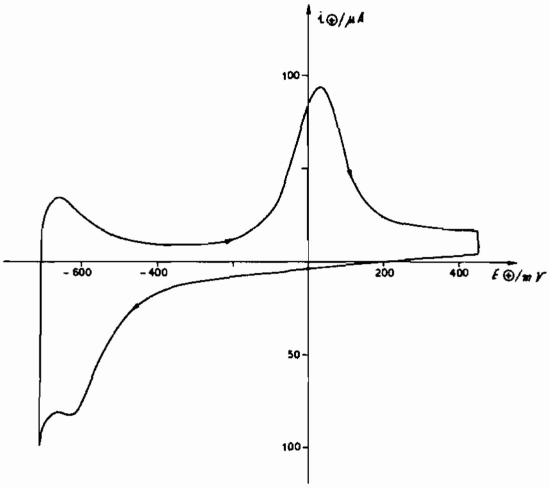


Figure 2. Cyclic voltammetric curve with platinum electrode for a $8 \times 10^{-4} M$ NH_4TcO_4, $0.1 M$ HCl–Borax (pH = 8) solution; scan rate 100 mV s^{-1}.

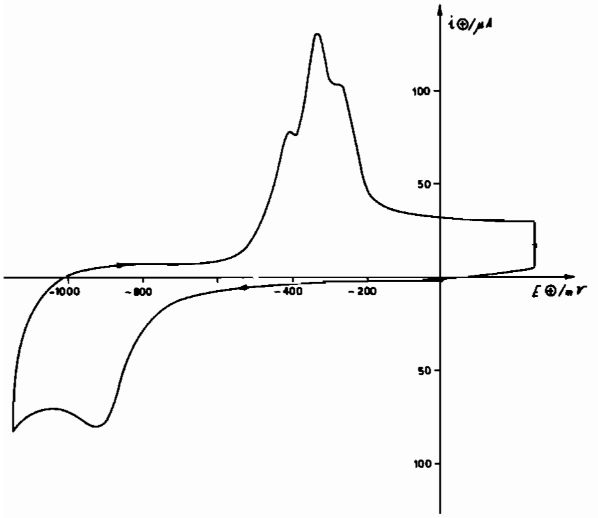


Figure 3. Cyclic voltammetric curve with platinum electrode for a 5 × $10^{-4}M$ NH_4TcO_4, 1*M* NaOH solution; scan rate 100 mV s^{-1}.

processes, because it is low both at high and at low scan rate, and reaches the maximum development at intermediate potential scan rates (100–200 mV s^{-1}).

Anodic and cathodic peaks were not diffusion controlled at any pH value.

The experimental data obtained from the voltammetric curves, recorded with a scan rate of 100 mV s^{-1}, at different pH values, are summarized in Table I; the peak potential reproducibility was evaluated to be about ± 10 mV.

The results obtained in HCl 3–10*M* solutions are not reported in Table I, because only the cathodic peak could be identified, but no associate anodic peaks could be observed in the available potential range, most probably because of the very high stability of technetium–chloro complexes.

In Figure 4 the dependence of the peak potential of the cathodic process from pH values is shown.

All the $(Ep)_c$ values lie on a straight line with a slope of 56 mV/pH.

Figure 5 shows the dependence of the anodic peak potential values from pH; from this plot three different types of behaviour can be obtained. In acid media a straight line, with a slope of about 56 mV/pH, can be drawn through the points representing the first anodic peaks.

The second anodic peaks of the acidic media and the ones obtained in the intermediate pH range, lie rather well on a straight line with a slope of 75 mV/pH. Finally, at high pH values, the peaks potentials of the first of the three anodic processes seem to lie again on a straight line with a slope of about 61 mV/pH.

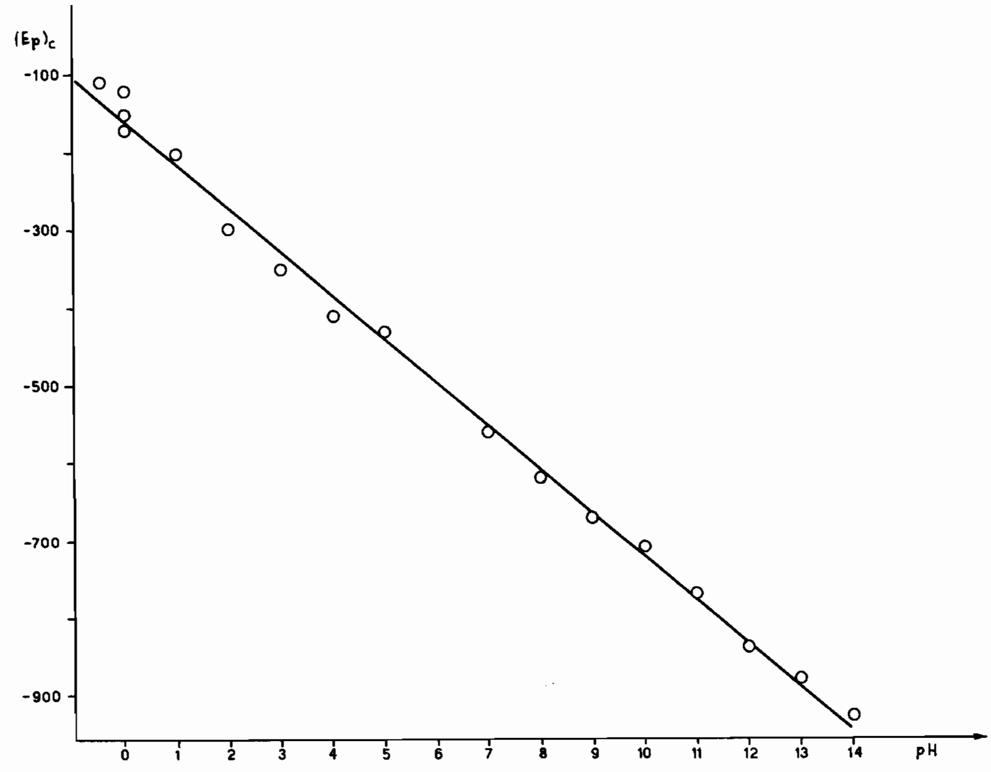


Figure 4. Dependence of the cathodic peack potential values, $(Ep)_c$, on pH.

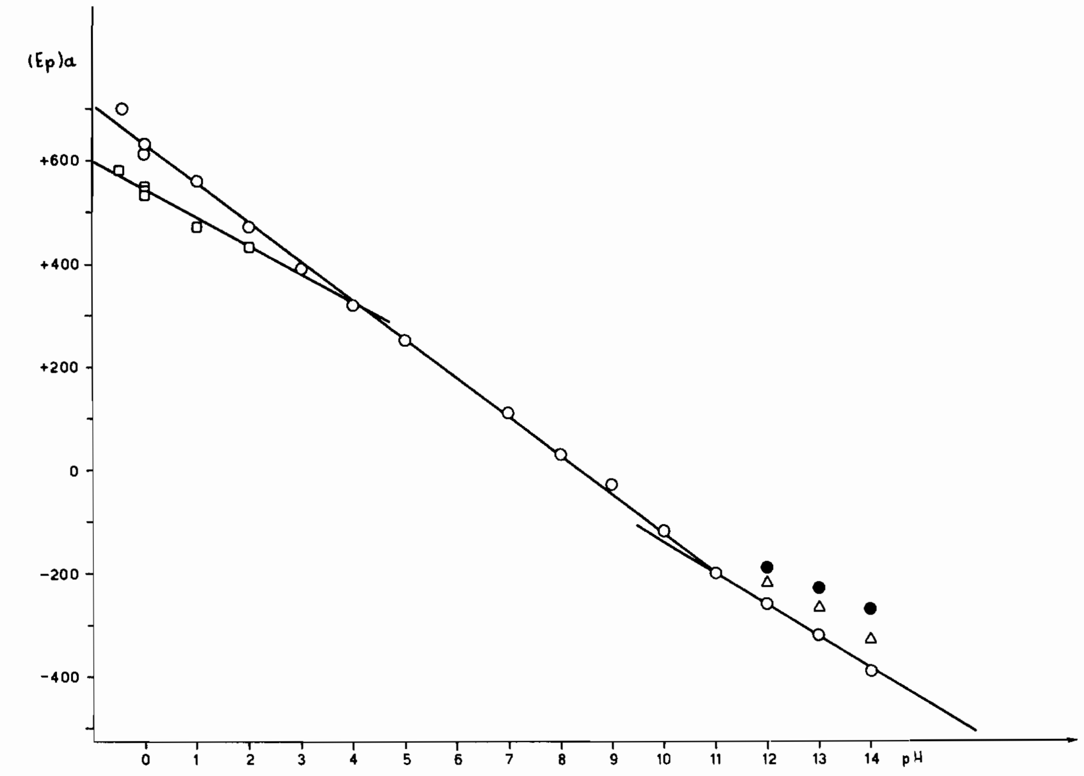


Figure 5. Dependence of the anodic peack potential values, $(Ep)_a$, on pH.

Coulometric experiments were unreliable owing to the simultaneous occurence of the solvent reduction.

The dependence of log i_t on t, for the electrolyses at controlled potential, was not linear, indicating that diffusion was not the rate determining step.

Controlled potential electrolyses performed at the $(Ep)_c$ values, in different media, allowed the recovery of a solid brown–black technetium oxide as a film on the electrode surface.

In concentrated HCl media (3–10*M*) the reduction product was soluble and the solution became progressively yellow–green.

In order to identify the reduction product, the following procedure was employed: at the end of the electrolyses the platinum foil of known weight was rinsed with twice distilled water, gently dried in a vacuum oven at 40° C for 30 minutes and then weighed. The electrode was put in a 1*M* H_2SO_4 solution of cerium sulfate of known concentration, where the oxide slowly dissolved. Back titrations with standard Fe^{II} solutions, indicated that the product was $TcO_2 \cdot 2H_2O$ for electrolyses carried out at pH values higher than 3. The end points of the titrations were detected potentiometrically.

The formation of TcO_2 was further checked by dissolving the brown–black product in a 10*M* HCl solution and recording the UV–visible spectrum; the obtained spectra strictly agreed with those reported in literature for $TcCl_6^{2-}$ ion.[20,23]

For electrolyses carried out at pH values lower than 3, the potentiometric titrations indicated an oxidation state for technetium intermediate between four and three.

The formation of Tc^{III} together with Tc^{IV} in concentrated HCl (3–10*M*) was established in the following way: known volumes of the yellow–green electrolyzed solution were titrated under nitrogen atmosphere with Ce^{IV} solution, after hydrolysis of technetium chloro complexes to the corresponding oxides with NaOH solution.

Aliquots of the same test solution were warmed in air until its colour became markedly yellow, ($TcCl_6^{2-}$), and then titrated with Ce^{IV} solution.

The amount of Ce^{IV} used in the first case was always larger (about 20%) than that used after the warming procedure. This difference demonstrated that in concentrated hydrochloric acid solutions both Tc^{III} and Tc^{IV} chloride complexes are formed.

In the above redox titrations, we assumed that Ce^{IV} was able to oxidize Tc^{III} and Tc^{IV} oxides to Tc^{VII}. This hypothesis is supported by the great difference between the redox potential of the Ce^{IV}/Ce^{III} couple in 1*M* H_2SO_4 and the peak potential value of the oxidation process of TcO_2. The oxidation number of the final product of the anodic reaction occurring at every pH values, has been checked to be seven in this way: the solutions obtained by dissolving anodically the technetium oxide, in solutions of the pure supporting electrolyte, gave UV spectra identical to those reported for the TcO_4^- ion.[20, 23]

Discussion

As reported above the reduction peak is always located at potential values corresponding to the reduction of hydrogen ions to adsorbed hydrogen, with the difference that the presence of TcO_4^- ions markedly increases this adsorption peak. In addition, the observed dependence of $(Ep)_c$ values on pH agrees (56 mV/pH instead of the theoretical 58 mV/pH) with that exhibited by the adsorption peak of hydrogen ions. These results suggest that the reduction of technetate (VII) ion takes place, on the platinum electrode, *via* adsorbed hydrogen atoms, namely the technetate(VII) ion undergoes a chemical reduction by hydrogen atoms. The presence of technetate(VII) seems thus to accelerate the rate of reduction of hydrogen ions by a fast following chemical reaction.

For the reduction of Te^{VII} to Tc^{IV} the overall scheme should be:

$$3H^+ + 3e \rightarrow 3\ H_{ads}$$
$$TcO_4^- + 3\ H_{ads} + H^+ \rightarrow TcO_2 + 2H_2O$$

On the other hand, if TcO_4^- ions underwent a direct electrochemical reduction, the dependence of $(Ep)_c$ values on pH should be higher than the experimental 56 mV/pH (77 mV/pH for a reversible behaviour).

Further demonstrations of the occurrence of a chemical reduction of Tc^{VII} by hydrogen atoms were gained from the following tests: on bubbling hydrogen gas into solutions of technetate(VII) ion, at any pH value, no appreciable reduction was detected; on the contrary, in the presence of platinum black the reduction of Tc^{VII} to TcO_2, or TcO_2 together with Tc_2O_3, took place. Furthermore, cyclic voltammetric tests carried out in a $10^{-3}M$ NH_4TcO_4, $0.1M$ But_4ClO_4, CH_3CN solution,[24] showed a reduction peak at potential values of −700 mV *vs.* an aqueous SCE. In the presence of hydrogen ions, which exhibit a well defined reduction peak at about 0 V *vs.* SCE,[25] the reduction of TcO_4^- ions occurs just at this potential, with the formation of a brown–black compound.

All the above reported findings agree with the well known procedure for the reduction of the technetate (VII) with zinc in hydrochloric acid.

The different anodic voltammetric behaviour of technetium at different pH values (Figure 5), can be explained assuming that in strong acid media Tc_2O_3 together with TcO_2 is formed, while, at pH values higher than 4, only TcO_2 is the reduction product. The titration data support this idea, and consequently the first anodic peak observed in acids media can be attributed to the process:

$$Tc_2O_3 + H_2O \rightarrow 2\ TcO_2 + 2H^+ + 2e$$

The experimental dependence from pH of the first $(Ep)_a$ value agrees rather well with the above reported anodic process which would require a slope of 58 mV/pH for a reversible behaviour.

The results of the redox titrations, the spectral data and the dependence from pH of the second anodic process in acid media, and also of the one exhibited up to pH 11, all indicate the anodic process:

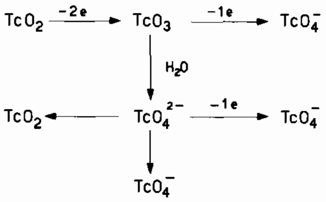
$$TcO_2 + 2H_2O \rightarrow TcO_4^- + 4H^+ + 3e$$

The formation of TcO_2 and Tc_2O_3 at pH values less than 3 and of TcO_2 at higher pH values, suggested in the present case by the different anodic behaviour, strictly agrees with the results of Salaria *et al.*,[6] who studied polarographically the cathodic behaviour of Tc^{VII} in the range $-0.6 \div 13.3$.

At the highest pH values (12–14) the anodic picture changes again: three peaks of different height are observed at different scan rates. However the initial and final products are, also in this case, TcO_2 and TcO_4^-.

For this very complicated behaviour only a tentative explanation can be advanced owing to the few data available from voltammetric and literature data, about the chemistry of technetium.[20,23,26,27] In addition, all the anodic electrode processes involve solid species, with variable activity during the voltammetric experiments.

The following reaction scheme agrees with the experimental results obtained at different scan rates:



According to this scheme, TcO_2 should be oxidized to TcO_3 at the first anodic peak, the obtained product can undergo two competitive reactions: a further electrochemical oxidation to TcO_4^- ion (third anodic peak) or to hydrolyze to TcO_4^{2-} species with a finite rate. This anion, in its turn, can disproportionate[20] to TcO_2 and TcO_4^- or can be oxidized to TcO_4^- ion (second anodic peak). At low scan rates, in fact, the third peak is almost undetectable because the TcO_3 hydrolysis process takes place at large extent and hence only the first two peaks are well formed.

The occurrence of the disproportion reaction of TcO_4^{2-} ion, reported in the literature,[20] is invoked here to account for the complete dissolution of the oxide film even at potential values corresponding to the first anodic peak.

At high scan rates, on the contrary, the hydrolysis process of TcO_3 should occur only at a very low extent and, consequently, the first and the third peaks are developed. In this connection Astheimer and Schwocau[12] found only two anodic peaks, for which no explanation was advanced, working with a stationary mercury electrode at low potential scan rates (17 mV s^{-1}) in NaOH 1*M*.

The $(Ep)_a$ potential values reported by the above cited Authors, are in the same potential range of those observed by us.

Our voltammetric results point out that the redox couple TcO_4^-/TcO_2 is completely irreversible at any pH value (Figures 1, 2, 3) and hence we disagree with the finding of Cobble *et al.*[28] who claimed for a reversible behaviour of the electrode $Pt/TcO_2/TcO_4^-$ from e.m.f. measurements in 0.05*M* HCl and 0.07*M* NaOH. However this disagreement could be explained taking into account the surface difference between our platinum electrodes and those employed by Cobble *et al.*[28], which were previously completely covered by a layer of TcO_2.

From all the data reported in the present paper, it comes out that the electrochemical behaviour of aqueous technetate(VII) ion on platinum electrodes is rather complicated, but nevertheless it is very similar to that exhibited on mercury electrodes: on platinum, the reduction to TcO_2 and Tc_2O_3 occurs *via* the intermediate hydrogen atoms, while these compounds are formed as charge transfer products on mercury.

The results obtained suggest the experimental conditions for a correct procedure for quantitative determinations of technetium(IV).[29] Finally, it can be noted that the formation of films of technetium oxides on the platinum surface can be utilized both for the recovery of this element from diluted aqueous solutions and for easy preparations of Tc^{IV} compounds, starting from technetate(VII) solutions.

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