Intermediate oxidation states of technetium in alkaline solutions

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ABSTRACT

The electrochemical reduction of pertechnetate ions (TcO_4^-) have been studied in strongly alkaline media (0.3 ÷ 10 M aqueous NaOH) using electrochemical (cyclic voltammetry (CV); chronoamperometry (CA), chronopotentiometry (CP)) and spectroelectrochemical (UV-Vis OTTLE and Au-SERS) techniques. Such obtained results show formation of two types of Tc(V) species as intermediates in the electrochemical reduction of the pertechnetates. The soluble Tc(V) forms, detected by means of UV-Vis measurements are relatively stable but disproportionate to Tc(IV) and Tc(VII). The other type of Tc(V) containing products is present at the electrode surface. The latter species were detected and characterized by a band at $700\,cm^{-1}$. The final products of the multistep reduction of the pertechnetates in $NaOH_{aq}$ are Tc(IV) compounds which composition depends on the electrolyte concentration. Thus, insoluble and adsorbed in the electrode surface TcO_2 is the main product in 0.3 M NaOH while soluble polymeric Tc(IV) are the prevailing species observed in 10 M NaOH.

1. Introduction

Technetium, as the lightest artificial element, is generated in large quantities (Tc-99: 6% fission products) during operation of a nuclear reactor. This long living radioisotope (half life time of $2.1 * 10^5$ years) can be extracted from acidic and alkaline aqueous solutions using solvent extraction methods [1]. Some fractions of the radioactive wastes generated in nuclear reactors, which, among other radioisotopes contain also Tc, are stored in liquid form as alkaline solutions in huge tanks [2,3]. Such solutions contain numerous elements in various chemical forms and oxidation states and this may lead to unwanted chemical reactions, including red-ox processes. The electrochemistry and red-ox processes of technetium are very complex due to the fact that this element can exist in many oxidation states [4]. Therefore, studies on electrochemistry of technetium started already in 1930s [5], with the special attention paid to the mechanism of TcO_4^- ions electroreduction process of ion in the alkaline solutions [6–10]. The latter process is complex and multistep and involves formation of Tc intermediates in various, potentially attractive for medicine and nuclear industry, oxidation states which red-ox properties must be understood.

Kissel and Feldberg [10] investigated pertechnenates reduction in 1 M NaOH with a special focus on disproportionation of technetates (VI), which are one of the intermediates in this process. They found that this disproportionation is very fast and competes with electroreduction of Tc(VI) ions to Tc(V). They concluded that the disproportionation of

Tc(VI) Eq. (2) can be experimentally studied only in presence of blocking agents, such as gelatin, and the overall reduction of pertechnetates is a two electron process. The standard redox potential for Tc(VII)/Tc(V) couple is equal to −0.60 (± 0.05)V [4]. Discussed processes can be described by the following Eqs. (1)–(3):

$$TcO_4^- + e^- \rightarrow TcO_4^{2-} \tag{1}$$

$$2TcO_4^{2-} \rightarrow TcO_4^- + TcO_4^{3-} \tag{2}$$

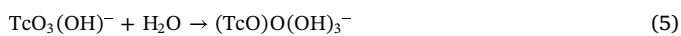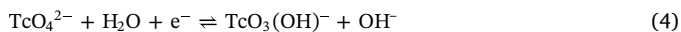$$TcO_4^{2-} + e^- \rightarrow TcO_4^{3-} \tag{3}$$

The rate constant of the disproportion described by Eq. (2) was determined by Deutsch et al. [8] using a pulse radiolysis technique and is equal to $2.48 \pm 0.05 \cdot 10^{10}\,M^{-1}\,s^{-1}$. The cyclic voltammograms recorded by these authors in 1 M NaOH reveal a single reduction wave at a potential of ca. −0.9 V and, subsequently, two smaller oxidation waves at ca. −0.8 V and −0.25 V (vs. SCE). A decrease in the scan rate of the electrode potential results in disappearance of the first oxidation peak (−0.8 V), an effect which can be attributed to a disproportionation process following an electrochemical step [11]. It was also shown in [8]. They found also that Tc(VI) absorbs visible light in the range of 500–600 nm (ε = ca. $250\,M^{-1}\,cm^{-1}$).

A slightly different scheme of pertechnetates reduction in alkaline media (0.01–0.1 M NaOH) was proposed by Founda et al. [9]. These authors assumed that Tc(VI) ions may undergo an electrochemical reaction coupled with a subsequent hydrolysis of the products according
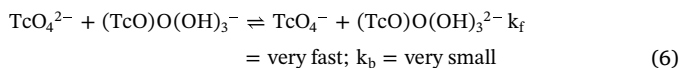
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to the Eqs. (4)–(5):

$$TcO_4^{2-} + H_2O + e^- \rightleftharpoons TcO_3(OH)^- + OH^- \tag{4}$$

$$TcO_3(OH)^- + H_2O \rightarrow (TcO)O(OH)_3^- \tag{5}$$

The disproportionation process has been presented in [9] as:

$$TcO_4^{2-} + (TcO)O(OH)_3^- \rightleftharpoons TcO_4^- + (TcO)O(OH)_3^{2-} \quad k_f$$
$$= \text{very fast}; \ k_b = \text{very small} \tag{6}$$
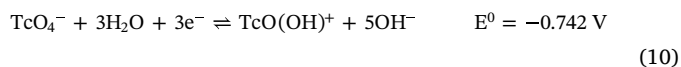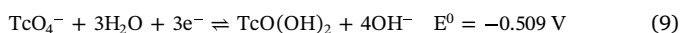
Tc(IV) compounds were the final products of pertechnetates reduction in 1 M NaOH but their structure (monomer or dimer) has not been identified [9].
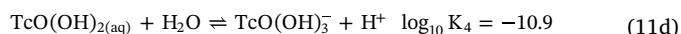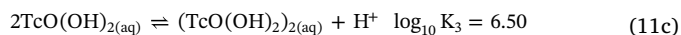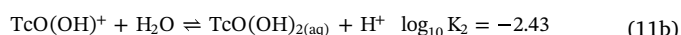
One possible pathway for the disproportionation of Tc(V) and its electroreduction to Tc(IV) in alkaline solutions can be described by Eqs. (7)–(8):

$$2HTcO_4^{2-} + H_2O \rightleftharpoons TcO(OH)_2 + TcO_4^{2-} + 2OH^- \tag{7}$$

$$HTcO_4^{2-} + 2H_2O + e^- \rightarrow TcO(OH)_2 + 3OH^- \tag{8}$$
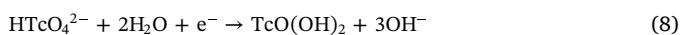
As it was discussed previously [12], the TcO^{2+} ions are stable only in strongly acidic media and in alkaline solutions they undergo a rapid hydrolysis leading to formation of technetium(IV) oxide/technetium(IV) oxohydroxide. Therefore, the hydrolysis processes should be included in the overall scheme of the reduction of TcO_4^- to Tc(IV) in non-acidic media, according to Eqs. (9)–(10) [13]:

$$TcO_4^- + 3H_2O + 3e^- \rightleftharpoons TcO(OH)_2 + 4OH^- \quad E^0 = -0.509 \text{ V} \tag{9}$$

$$TcO_4^- + 3H_2O + 3e^- \rightleftharpoons TcO(OH)^+ + 5OH^- \qquad E^0 = -0.742 \text{ V} \tag{10}$$

A series of equilibria between different forms of Tc(IV) are well documented in the literature [4] and can be presented by Eqs. (11a)–(11d). It is likely, however, that these equations do not fully reflect discussed processes as they do not take into account formation of polymeric forms of Tc(IV). The electrochemistry of the latter species seems to be of key importance in understanding the redox behaviour of technetium in aqueous media.

$$TcO^{2+} + H_2O \rightleftharpoons TcO(OH)^+ + H^+ \quad \log_{10} K_1 = -1.37 \tag{11a}$$

$$TcO(OH)^+ + H_2O \rightleftharpoons TcO(OH)_{2(aq)} + H^+ \quad \log_{10} K_2 = -2.43 \tag{11b}$$

$$2TcO(OH)_{2(aq)} \rightleftharpoons (TcO(OH)_2)_{2(aq)} + H^+ \quad \log_{10} K_3 = 6.50 \tag{11c}$$

$$TcO(OH)_{2(aq)} + H_2O \rightleftharpoons TcO(OH)_3^- + H^+ \quad \log_{10} K_4 = -10.9 \tag{11d}$$

It is worth noting that formation of anionic Tc(IV) forms predicted by Eq. (11d) should be facilitated in strongly alkaline media where the presence of high concentration of hydroxyl ions shifts the following equilibrium towards formation of $TcO(OH)_2$.

$$\frac{[TcO(OH)_3^-]}{[TcO(OH)_2]} = \frac{K_4}{K_w} * [OH]^- = 10^{3.1} * [OH^-] \tag{12}$$

One may conclude based on Eq. (11c) that a dimerization process or, most likely, a further polymerisation of Tc(IV) species is the possible process of technetium redox species evolution.

It should be stressed that the red-ox reactions of pertechnetates in alkaline media are accompanied by formation of numerous other than TcO_2, technetium species whose structure and formation pathways are not yet fully understood.

In this work the spectroelectrochemical (UV-Vis, SERS) and electrochemical (CV, CA, CP) techniques have been applied to study the redox behavior of technetium species in alkaline media. The measurements were carried under stationary and hydrodynamic conditions.

2. Experimental

All experiments described in this paper were performed at 298 K in 0.3–10.6 M NaOH aqueous solutions prepared using high purity distilled water (Millipore®) and high purity chemicals. The solutions were prepared by dissolving potassium pertechnetate $K^{99}TcO_4$ (Forschungszentrum Dresden-Rossendorf - Institute of Radiopharmacy) in NaOH solutions (POCh, Poland). The concentrations of $K^{99}TcO_4$ solutions were 1 mM (or 3.5 mM) and 0.5 mM for the spectro-electrochemical (UV-Vis or SERS) and electrochemical experiments, respectively. Two types of cells were used: a thin layer one in the UV–Vis experiments (finite diffusion conditions) and a cell with the volume of 100 ml in the electrochemical studies (semi-infinite diffusion conditions). Optically transparent thin layer electrodes with Reticulated Vitreous Carbon (RVC, ERG Aerospace Corporation, USA) as the working electrode material were used in spectroelectrochemical experiments. A rotating ring-disc electrode (RRDE) with a polycrystalline gold disk and ring in a Teflon sleeve (RRDE AFER8AUAU) was used in electrochemical experiments (cyclic voltammetry, CV) on reduction of pertechnetates ions under stationary and hydrodynamics conditions The diffusion coefficient of pertechnetates in concentrated alkaline solutions was estimated using a procedure similar to that described previously for concentrated sulfuric acid electrolytes [12]. The viscosity of all NaOH solutions was calculated on the basis of the literature data [14,15]. All the experiments were carried out in a three electrode system with a Pt mesh and Ag/AgCl$_{(KClsat.)}$ or Hg,HgO (0.1 M NaOH) serving as a counter and a reference electrode, respectively. The liquid junction potential between saturated KCl and NaOH or 0.1 M NaOH and 0.6, 4 or 10 M NaOH solutions can be calculated on the basis of the literature data [16,17]. The electrochemical measurements were performed using an Autolab (PGSTAT128N) electrochemical analyzer which was coupled with a MultiSpec 1500 (Shimadzu) spectrophotometer in spectroelectrochemical measurements. The Raman/SERS spectra were recorded using a Labram HR800 (Horiba Jobin Yvon) spectrometer working in a backscattering configuration and coupled with a confocal microscope. The SERS spectra were accumulated during double scans with the integration time of 300 s. A He-Ne (632.8 nm) laser was used as the excitation source with the laser beam power at the sample surface reduced to 1 μW. The rough surface of the gold electrode used in these studies was prepared according to procedure described in [18]. More details about the spectroelectrochemical Raman experiments and SERS substrate preparation can be found in our previous paper [19].

3. Results and discussion

Fig. 1 presents cyclic voltammograms recorded at a scan rate of 1 mV/s with a RVC-OTTL electrode in 0.3 and 10 M NaOH containing 1 mM of KTcO$_4$. The reduction of pertechnetate ions in both solutions leads to a weak increase of cathodic current at potentials lower than -0.6 V. According to the literature [9] the reduction of TcO_4^- ions leads to generation of technetium species in various oxidation states (from +VI to +IV). The Tc(VI) compounds are very unstable and immediately disproportionate to Tc(VII) and Tc(V). The potentials of the TcO_4^- reduction currents are shifted towards more positive values when the concentration of NaOH increases.

When reduced Tc species formed during electrochemical reduction of pertechnetates are subsequently electrochemically oxidation in 0.3 M NaOH a broad and poorly shaped anodic wave is formed at potential range -0.5 V–-0.1 V. This signal becomes more flat and less visible when NaOH concentration increases up to 10 M. This suggests a lower efficiency of the pertechnetates electroreduction and subsequent oxidation of such formed reduced Tc species in strongly concentrated alkaline media. This effect can be attributed to blocking of the electrode surface by the hydroxyl ions. The shape of chronovoltabsorbommograms calculated for selected wavelength of 244 nm (TcO_4^-), 460 nm (Tc(V) or Tc(VI?)) and 495 nm (Tc(IV)$_{polymeric}$) show that final products of pertechnetates electroreduction depend on alkaline solution concentration. The negative wave observed on the voltabsorbommogram at