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*Short communication*

# Diffusion coefficients of $Ta^{5+}$ and $Ti^{4+}$ ions in methanesulfonic acid–methanol solutions

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## 1. Introduction

Valve metals, like tantalum and titanium, are finding increasing applications, especially in biomedical applications and in very corrosive environments such as chloride containing solutions. To describe electrochemical processes involving metals, knowledge of the diffusion coefficients of the metal ions is necessary. Valve metals are polished in organic solvents containing strong acids; for instance, tantalum [1] and titanium [2] in sulfuric-methanol electrolytes, but the diffusion coefficients of their metal ions are unknown [2]. To determine the diffusion coefficient of $Ta^{5+}$ and $Ti^{4+}$ ions in practically water-free conditions, a methanesulfonic acid (HMSA)–methanol solution containing a small concentration of these ions is used. Normal electrochemical methods cannot be applied for these metals. To determine the diffusion coefficient of species an old method, the diaphragm method, can be successfully applied [3]. This method consists in separating two homogeneous bodies of solution by an indifferent separator with pores of visible or microscopic size, confining the linear diffusion gradient within this membrane.

## 2. Experimental details

Voltammetric experiments were carried out to determine whether the $Ti^{4+}$ and $Ti^{5+}$ ions could be reduced.

An H-shaped cell with two compartments separated by a PTFE filter (pore size 0.45 $\mu$m) with a diameter of 13.5 mm and a thickness of about 0.25 mm was used. Each compartment ($S_1$, $S_2$) was filled with 100 cm$^3$ HMSA–methanol (10–90 wt%) solution; initially, $S_1$, contained 11.6 mM $Cu^{2+}$, 13.8 mM $Ta^{5+}$ and 10.8 mM $Ti^{4+}$ and the other compartment, $S_2$, contained no metal ions. $Cu^{2+}$ was used as reference ion, since its diffusion coefficient has been determined by an electrochemical method [4]. A thermostat was used to keep the temperature of both solutions at 298 K.

The HMSA–methanol solution with the three types of metal ions was made by mixing three HMSA–methanol (10–90 wt %) solutions each containing only one type of metal ion. A $Cu^{2+}$ solution was prepared by dissolving Copper(II) carbonate basic ($CCuO_3 \cdot CuO_2H_2$, Acros Organics). A $Ta^{5+}$ solution was made by anodic dissolution of tantalum metal (99.9%Ta) at a current density of 100 mA cm$^{-2}$. The same procedure was applied to prepare a $Ti^{4+}$ solution.

Metal analyses were carried out with an inductively coupled plasma instrument (Spectrociros$^{ccd}$ ICP). Standard solutions were prepared with copper(II) carbonate basic, tantalum(V) ethoxide ($C_{10}H_{25}O_5Ta$, Fluka) and titanyl acetylacetonate ($C_{10}H_{14}O_5Ti$, Merck-Schuchardt). The HMSA–methanol (10–90 wt %) samples, were analysed after 125 times dilution with a HMSA–methanol–water (1-9–90 wt %) solution.

After filling of the cell with the two different solutions ($S_1$ and $S_2$), samples of the same volume of both solutions were taken after 0, 8, 24, 48 and 149.5 h. The metal ion concentrations in the dilute samples from solution $S_2$ were below or close to the detection limit. Only the dilute samples taken at 48 and 149.5 h showed well-determinable concentrations of $Cu^{2+}$, $Ta^{5+}$ and $Ti^{4+}$.

## 3. Results and discussion

It was found that no clear reduction waves are obtained and even the deposition of the metals Ta and Ti from aqueous and organic solvent solutions is impossible. Using Fick's first law for a system with two equal volumes of solution McBain and Liu [3] derived a relation for the metal ion concentration $c_2$ in solution $S_2$:

$$\log\left(\frac{c_{1,0}}{c_{1,0} - 2c_2}\right) = K_{\text{cell}} D t_{\text{e}}$$

where $c_{1,0}$ and $c_2$ are the concentrations of the metal ion in solution of $S_1$ at $t_e = 0$ (mol m$^{-3}$) and $S_2$ at $t_e$

(mol m$^{-3}$), respectively. $K_{cell}$ is the cell constant (m$^{-2}$), where $K_{cell} = A_s/V_2d_s$; $A_s$ is the effective area of separator; $d_s$ is the thickness of separator; $D$ is the diffusion coefficient of metal ions; $V_2$ is the volume of solution $S_2$; and $t_e$ is the elapsed time (s).

The cell constant $K_{cell}$ was determined by measuring the diffusion of a standard substance such as 11.6 mM Cu(II) in 10 wt % HMSA – 90 wt % methanol. In this medium the diffusion coefficient of Cu(II) is known to be $5.33 \times 10^{-10}$ m$^2$ s$^{-1}$ at 293 K [4]. Taking into account that, within a narrow range of temperature the temperature coefficient of the diffusion coefficient for most ions is in the neighbourhood of 2 per cent per degree [5], the diffusion coefficient of Cu(II) can be estimated at $5.86 \times 10^{-10}$ m$^2$ s$^{-1}$ at 298 K. The calculated cell constants were found to be 561 and 570 m$^{-2}$ for $t_e$ = 48 and $t_e$ = 149.5 h, respectively; the value for the cell constant was then taken to be 565 m$^{-2}$.

Since the standard deviation in the concentrations at $t_e$ = 48 h is clearly higher than that at $t_e$ = 149.5 h, for instance about 5.6% at $t_e$ = 48 h and 0.5% at $t_e$ = 149.5 h for Ta$^{5+}$, the results at $t_e$ = 149.5 h are the most reliable and are used to determine the diffusion coefficient.

Using the cell constant of 565 m$^{-2}$, it was found that the diffusion coefficient for Ta$^{5+}$ is $5.67 \times 10^{-10}$ m$^2$ s$^{-1}$ and that of Ti$^{4+}$ is $6.28 \times 10^{-10}$ m$^2$ s$^{-1}$, both at 298 K. This means that the diffusion coefficients for Cu$^{2+}$, Ta$^{5+}$ and Ti$^{4+}$ are of the same order of magnitude and, taking into account the large difference in the charge of the metal ions, it is likely that complexation of these ions takes place.

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