ELECTRODE KINETICS OF THE Ti(IV)/Ti(III) SYSTEM IN WATER AND IN WATER–DIMETHYLFORMAMIDE AND WATER–DIMETHYL SULFOXIDE MIXED SOLVENTS

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The electron transfer rate constants in the reduction of Ti^{4+} and oxidation of Ti^{3+} in water and in water–DMF and water–DMSO mixtures were determined by square-wave polarography and by analysis of the DC and pulse polarographic curves. The two reactions occur at different potentials due to the rapid consecutive transformation of the primary product of the electrode reaction. Thus the rate constants are no standard rate constants, and depend on the method employed. The effect of the organic co-solvent varies for both reactions as a consequence of dependence of the degree of electrode coverage on potential. Generally, the adsorbed organic substance exerts an accelerating catalytic effect.

Within our study of the solvent effect on electrode reaction kinetics, we examined previously the one-electron transfer in the Eu^{3+}/Eu^{2+} and V^{3+}/V^{2+} systems where both the oxidized and reduced species are present in solution. We employed water in mixtures with organic solvents, either less basic[1,2] or more basic[3] than water. Such systems were objects of study by other authors as well[4–6]. The $Ti^{4+} + e \rightarrow Ti^{3+}$ one-electron transfer is another system whose investigation is of interest; this is the subject of the present paper.

The kinetic parameters of the Ti^{4+}/Ti^{3+} redox system have been examined in the presence of some complexing agents[7,8], whereas in non-complexing systems, only the cathodic charge transfer coefficient has been determined[7]. The polarographic behaviour of Ti^{4+} in sulfuric acid solutions was the subject of paper[9], which explained the wave splitting in terms of equilibria between hydroxo-aqua complexes of various composition. The choice of a suitable method for determining the electrode reaction rate constant primarily depends on the level (order of magnitude) of the rate constant. From among available techniques, we selected square-wave polarography for fast phenomena and DC and pulse polarography for slower (irreversible) phenomena.

EXPERIMENTAL

Organic solvents were prepared as described previously[1,2]. Solution of Ti^{4+} was prepared by dissolving TiO_2 in sulfuric acid and adjusted to a concentration of 0.2 mol l^{-1} in 5 M H_2SO_4. Solution of Ti^{3+} was prepared from an acid Ti^{4+} solution in a Jones reductor with amalgamated zinc[10] under nitrogen, and added directly to the other components in the measuring vessel, prior freed from oxygen by nitrogen purging.

The resulting solution contained Ti^{3+} or Ti^{4+} in a concentration of 2 mmol l^{-1} in a medium of 0.1 M H_2SO_4 and 0.1 M $NaClO_4$ in a mixed solvent with 0 to 80% organic component. The DC and pulse polarographic curves were measured on a PA4 polarographic analyzer (Laboratorni pristroje, Prague). The pulse width was 100 ms, the sampling window was centered at 90 ms. The square-wave polarographic measurements were made with an OH 104 instrument (Radelkis, Budapest) applying a square-wave voltage frequency of 200 Hz. The working temperature was 25 °C. The three-electrode connection was used, employing a mercury drop working electrode and a mercurous sulfate reference electrode with an Na_2SO_4 saturated solution; mercury bottom served as the auxiliary electrode. To facilitate comparison with other data, all potentials in this paper are reported versus saturated calomel electrode. The rate constants calculated at a constant potential difference against the ferricinium/ferrocene (Fic/Foc) system (to eliminate the effect of the different diffusion potential at the aqueous reference electrode/mixed solvent interface), the potential of the latter reference system vs MSE was measured by cyclic voltammetry at a platinum electrode; this is an approach which has been applied by other authors as well[11,12].

RESULTS

The rate constants of the electrode reaction of titanium in aqueous solutions were determined by square-wave polarography, both for the reduction of Ti^{4+} and oxidation of Ti^{3+}. The procedure for obtaining the standard rate constant k_s and standard potential E^0 based on the Tamamushi–Matsuda theory[13] has been reported previously[1]. The diffusion coefficients were calculated from the limiting polarographic currents of diffuse nature, using the extended Ilkovic equation[14]. The k_s and E^0 data obtained from square-wave polarographic measurements and the diffusion coefficients derived from the polarographic curves are given in Table I.

TABLE I
Standard rate constants (k_s), potentials (E^0) and diffusion coefficients of titanium in aqueous medium (0.1 M H_2SO_4 + 0.1 M $NaClO_4$) derived from square-wave polarographic measurements

Reaction	$k_s \cdot 10^4$, cm s^{-1}	E^0, V	$D \cdot 10^6$, cm^2 s^{-1}
$Ti^{4+} + e \rightarrow Ti^{3+}$	5.4	−0.77	4.9
$Ti^{3+} - e \rightarrow Ti^{4+}$	5.3	−0.20	5.2

When the organic solvent was added, the electrode reaction rate decreased to the extent that square-wave polarography was inapplicable to the determination of the rate constant. Evaluable results were only obtained after additionally increasing the organic solvent content. Moreover, Ti^{3+} oxidized spontaneously in the water–DMSO system. (In some circumstances, Ti^{3+} is capable of reducing ClO_4^- to Cl^-, ref.[15].) The standard rate constants obtained by square-wave polarography for the reduction of Ti^{4+} in the mixed solvents are given in Table II.

Since square-wave polarography failed to afford the rate constants over a wide region of organic co-solvent concentrations, the Koutecky method[16,17] of polarographic curve evaluation was also employed. The results were verified by pulse polarography[18]. The rate constants in the water–DMF system were evaluated from both the anodic and cathodic curves. The rate constants derived from the points of intersection of the linear $\ln k_s$ vs E plots for the condition $k_{red} = k_{ox}$, the apparent standard potentials E_{app}^0 corresponding to the points of intersection, and the charge transfer coefficients are given in Table III. The E_{app}^0 values served as the standard potentials in the rate constant calculation based on the pulse polarographic measurement (k_{NP}). The dependence of the rate constant on composition is shown in Fig. 1.

TABLE II
Standard rate constants ($k_s \cdot 10^4$) of titanium in mixed solvents derived from square-wave polarographic measurements; the maximum error is 0.2

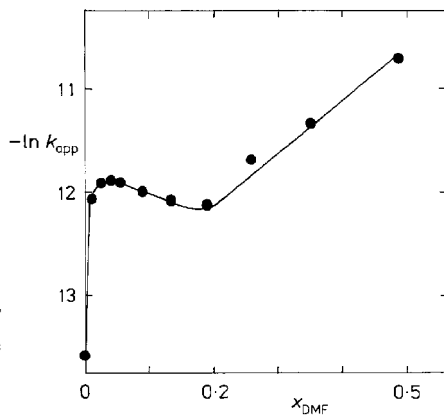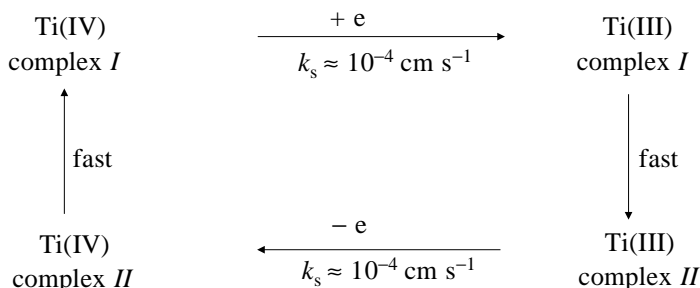| System	Organic fraction, %				
	40	50	60	70	80
DMF–water	–	–	–	3.1	3.2
DMSO–water	4.4	4.7	4.8	4.9	5.1

FIG. 1
Dependence of $\ln k_{app}$ of titanium on the DMF mole ratio at the potential corresponding to the point of intersection of the Tafel straight lines (E_{app}^0)

The values obtained from the reduction waves of Ti^{4+} in the water–DMSO systems are given in Table IV. Since Ti^{3+} cannot be prepared in the solution containing DMSO, the kinetic data were calculated for the potentials corresponding to the points of intersection of the Tafel dependences in aqueous medium.

DISCUSSION

The E^0 values (Table I) obtained by square-wave polarography indicate that different equilibria establish during the oxidation and during the reduction. This is consistent with the polarographic study by Habashy[9]. The system can be represented by Scheme 1.

Ti(IV) complex *I* $\xrightarrow{\substack{+\ e \\ k_s \approx 10^{-4}\ \text{cm s}^{-1}}}$ Ti(III) complex *I*

fast   fast

Ti(IV) complex *II* $\xleftarrow{\substack{-\ e \\ k_s \approx 10^{-4}\ \text{cm s}^{-1}}}$ Ti(III) complex *II*

Scheme 1

Table III

Kinetic parameters of the Ti^{3+}/Ti^{4+} system in water–DMF mixtures obtained by the method[15,16]

DMF, %	x_{DMF}[a]	$-E^0_{app}$ V	$k_{app} \cdot 10^{6,b}$ cm s^{-1}	$k_{NP} \cdot 10^{6,c}$ cm s^{-1}	$D_{ox} \cdot 10^{6,d}$ cm^2 s^{-1}	$D_{red} \cdot 10^{6,d}$ cm^2 s^{-1}	α^e	β^e
0	0	0.402	1.2	1.3	4.89	5.21	0.43	0.77
5	0.012	0.314	5.7	8.1	4.51	4.94	0.39	0.66
10	0.025	0.317	6.5	9.0	3.97	4.38	0.42	0.65
15	0.040	0.318	6.8	9.6	3.44	3.88	0.43	0.65
20	0.055	0.318	6.6	9.9	3.07	3.34	0.45	0.68
30	0.091	0.323	6.2	9.1	2.56	2.95	0.47	0.69
40	0.134	0.327	5.7	8.5	2.18	2.50	0.47	0.69
50	0.189	0.334	5.5	9.8	1.86	2.17	0.47	0.74
60	0.258	0.341	8.4	11.8	1.61	1.96	0.48	0.77
70	0.352	0.347	12.0	21.4	1.61	2.00	0.46	0.77
80	0.482	0.349	20.9	28.4	1.69	2.04	0.45	0.73

[a] x DMF mole ratio; [b] k_{app} the apparent rate constant derived from the intersection of the Tafel dependences; [c] k_{NP} the rate constant derived from pulse polarographic measurement; [d] D the diffusion coefficient; [e] α and β cathodic and anodic charge transfer coefficients, respectively.

In this scheme, the complex of tetravalent titanium (*I*), which is generally octahe-drally coordinated, involves mainly hydroxo complexes. According to Beukenkamp and Herrington[19], Ti(O)H and Ti(OH)$_3$HSO$_4$ are the major species in systems ap-proaching those used by us, the remaining coordination sites being occupied by mole-cules of water[19], whereas Nazarenko and coworkers[20] suggest that Ti(OH)$_4$ is the predominating species, followed by Ti(OH)$_3^+$. The stable complex of trivalent titanium (*II*) will be mainly constituted by the monohydroxo complex Ti(OH)(H$_2$O)$_5^{2+}$ (refs[15,21]).

The Ti(IV) species accepts an electron and reduces to the corresponding reduction product. The standard potential of this redox system in aqueous solution is $E^0 = -0.77$ V. A consecutive reaction leads to the more stable Ti(III) species (complex *II*). The reverse reaction by the same pathway would be energy demanding; the oxidation of the species goes through a more favourable pathway, viz. electron donation with a sub-sequent reaction. Thus the cathodic and anodic charge transfer coefficients α and β, respectively, characterize two different electrode reactions. This concept is corrobor-ated by the fact that the sum of the two coefficients obtained from the slopes of the Tafel dependences for the reduction and for the oxidation is greater than 1 (Table III), the error of determination being 0.02. The consecutive reactions which are supposed to occur and are apparently very fast may be detectable by very fast cyclic voltammetry only. In our cyclic voltammetry measurements applying scan rates up to 10 V s^{-1}, no direct products of reduction of tetravalent titanium of direct oxidation products of tri-valent titanium could be traced. The above concept is consistent with the results from square-wave polarography, which – as a rather rapid method (superimposed voltage

TABLE IV
Cathodic rate constants k_k and k_{NP} derived from polarographic measurements and pulse polarographic measurements at E^0_{app} in aqueous solution

DMSO, %	x	$k_k \cdot 10^5$ cm s^{-1}	$k_{NP} \cdot 10^5$ cm s^{-1}	$D_{ox} \cdot 10^6$ cm^2 s^{-1}	α
0	0	0.12	0.14	4.89	0.43
5	0.013	5.2	4.5	4.47	0.45
10	0.027	7.8	8.2	4.09	0.47
15	0.043	9.6	8.3	3.52	0.51
20	0.059	10.0	9.5	3.23	0.53
30	0.098	8.2	8.7	2.44	0.54
40	0.144	6.9	7.4	2.02	0.57
50	0.202	5.8	5.9	1.57	0.62
60	0.275	5.5	5.5	1.38	0.63
70	0.371	5.8	6.2	1.23	0.62
80	0.503	7.1	7.6	1.32	0.61

frequency 200 Hz) – gave rate constants two orders of magnitude higher that as obtained based on DC polarographic measurements, from the points of intersection of the Tafel straight lines (Table I vs Table III).

Due to the occurrence of two different equilibria in the oxidation of Ti^{3+} and reduction of Ti^{4+}, the point of intersection of the Tafel straight lines does not agree with the true standard potential obtained by the Koutecky method; thus the rate constants derived are no standard rate constants. An approach applied usually to such cases was therefore used to compare the effect of increasing organic co-solvent content on the electrode reaction rate, and the rate constants were calculated and compared for a suitably chosen constant potential[22,23]. The rate constants were calculated at the true standard potential in aqueous solution obtained by square-wave polarography for the oxidation and reduction (Table I). The dependences of logarithms of the rate constants (calculated for that potential) on the solvent composition are shown in Fig. 2. The rate constant value at that potential is affected by the liquid potential at the interface of the reference electrode with the solution measured. Therefore, the rate constants at a constant potential with respect to the reversible peak of the Fic/Foc system in the same solvent are also shown in Fig. 2.

The dependences of the rate constant logarithms (at a constant potential with respect to that of the Fic/Foc system in the same solvent) on the solvent composition have different shapes for the oxidation and reduction (curves *2* and *4* in Fig. 2). The standard potential of reduction of Ti^{4+} at which the corresponding rate constants were calculated lies in the potential region of maximum adsorption of DMF on the electrode surface, as indicated by the capacity curves for water–DMF mixtures measured by us previously. The standard potential of oxidation of Ti^{3+}, on the other hand, lies in the region of a steep increase of the double-layer capacity. Hence, the reduction and oxidation processes take place at quite different interfaces. The shape of the dependence for the reduction of Ti^{4+} approaches that for the reduction of Eu^{3+} in the water–DMF system
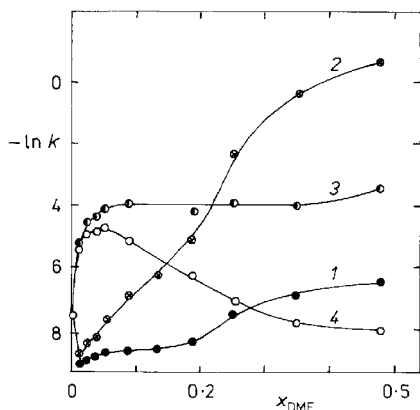

F$_{IG}$. 2

Dependence of ln k of the electrode reaction of titanium on the DMF mole ratio at the standard potential in aqueous solution. For the oxidation of Ti^{3+}: *1* with respect to SCE, *2* with respect to the Fic/Foc system in aqueous solution; for the reduction of Ti^{4+}: *3* with respect to SCE, *4* with respect to the Fic/Foc system in the same medium

observed by Maksimyuk and coworkers[22]; the authors explained the shape in terms of catalysis of the electrode reaction by the adsorbed organic co-solvent.

Figure 3 shows the dependences of the rate constants of reduction of Ti^{4+} on composition in the water–DMSO (Table IV) and water–DMF systems. While the reduction is somewhat faster in the DMSO system than in the DMF system, the curves are similar in shape, hence, the effects of the organic co-solvent are similar as well.

Comparison of the shapes of dependences measured at a constant potential with respect to the reference electrode with those measured at a constant potential difference against the Fic/Foc system (Fig. 2) demonstrates a significant effect of the diffuse potential at any electrochemical measurement in aqueous–organic mixed systems.
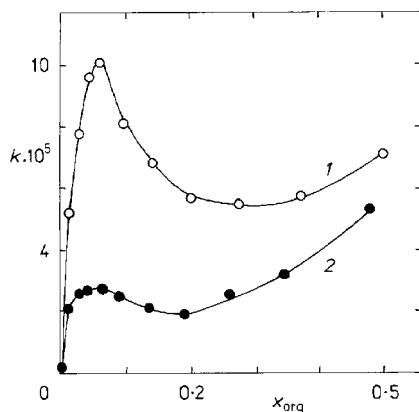

FIG. 3
Comparison of dependences of the rate constants of Ti^{4+} reduction in the water–DMSO (*1*) and water–DMF (*2*) systems

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