
ELECTRODE KINETICS OF THE SYSTEM V(III)/V(II) IN AQUEOUS DIMETHYLSULPHOXIDE

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Dedicated to the memory of Prof. J. Heyrovský on the occasion of his centenary.

The rate constants for the reduction of V(III) and oxidation of V(II) were measured on a mercury electrode in water and water-dimethylsulphoxide mixtures. Their dependence on the concentration of DMSO differs from that in mixtures of water with an organic solvent of lower basicity. This can be attributed to the existence of different solvates of vanadium in solutions and to different values of the rate constant for these solvates on the electrode surface at different coverages with the organic component. The influence of DMSO both in the primary solvation sphere and in the electrode double layer on the electrode reaction rate is discussed.

Our preceding works^{1,2} dealt with the study of the kinetics of the electrode reaction $V(\text{III}) + e \rightleftharpoons V(\text{II})$ in mixture of water with an organic solvent which was less basic than water (acetone, acetonitrile). The characteristic dependence of the standard rate constant on the solvent composition (with a round minimum) was treated quantitatively on the assumption that solvate molecules are exchanged during transfer from the solution into the double layer and that an equilibrium exists between two types of solvated ions in solution. The dependence of the rate constant on the solvent composition is influenced both by the permittivity of the organic component, characterizing the ability to replace water molecules from the double layer, and by its donor number (DN), characterizing the ability to replace water molecules in ion solvation spheres.

The present work deals with the kinetics of the electrode reaction in mixtures of water with an organic component that is more basic than water. Here, the dependence of the standard rate constant on the solvent composition is different: the rate constant increases already with small additions of the organic solvent and its concentration dependence shows a local maximum and minimum (Fig. 3). Its changes, however, do not exceed an order of magnitude, in contrast to the systems studied earlier^{1,2}. The dependence mentioned can be elucidated on the basis of a photometrical study of changes of V(II) complexes during increasing the concentration of the organic

solvent. A similar course was observed for reduction of vanadium in aqueous dimethylformamide⁴ and for reduction of Eu(III) in mixtures of water with DMF (ref.³) or with DMSO (ref.⁵).

EXPERIMENTAL

DMSO was purified by the method described earlier⁶ and contained no more than 0.1% of water. $V(\text{ClO}_4)_2$ was prepared by electroreduction of $\text{VO}(\text{ClO}_4)_2$ (prepared from V_2O_5 according to ref.⁷) in an acidified aqueous solution in the absence of air on a mercury pool electrode. The solution was transferred in nitrogen atmosphere into a tempered measuring cell and mixed with the other components. The resulting solution contained 1 mM V(II) and 0.2 M HClO_4 in aqueous DMSO of the desired composition. Solutions of V(III) were prepared by oxidizing the V(II) solutions with atmospheric oxygen. The concentration of different oxidation states of vanadium ions was checked polarographically. Polarographic curves were recorded with a Radelkis OH 105 type polarograph in the three-electrode mode. A Hg_2SO_4 /saturated Na_2SO_4 reference electrode was used.

Square-wave polarographic curves were recorded with a Radelkis OH 104 type polarograph in the same mode. Measurements for oxidation of V(II) and reduction of V(III) were carried out independently. The standard rate constants were determined from the results on the basis of the Tamamushi and Matsuda theory⁸. The experimental ratio of the peak current on the square-wave polarogram to the limiting dc polarographic current was compared with the value calculated from the diffusion coefficient, transfer coefficient, and a set of chosen rate constant values at the standard potential. This method has the advantage that the value of E^0 need not be calculated explicitly and that eventual errors in the reactant concentration are eliminated.

Absorption spectra of the V(II) complex with various ratios of water to DMSO were measured in nitrogen atmosphere with a photometer Shimadzu UV 3000 in the range of wave lengths 240–330 nm (above absorption of DMSO). The concentration and acidity of the solutions were the same as in the electrochemical measurements.

RESULTS

In Fig. 1 are shown the absorption curves of the V(II) complex in aqueous solution and in solutions containing DMSO. (To eliminate absorption of DMSO, the region below 250 nm was not considered.) The character of the changes of the spectra suggests a gradual change of the ligands (substitution of DMSO for water). To study these changes, use was made of the absorbance values measured at 260, 270, 280, and 290 nm: for each concentration of DMSO, the ratio of absorbance to that of a solution containing 50% of DMSO at the same wave length was calculated. Mean values of these relative absorbances from the data at the four wave lengths indicated are given in Fig. 2 as functions of the DMSO concentration.

The measured values of the standard rate constant of the electrode reaction (average of the values for oxidation of V(II) and reduction of V(III)) are given in Fig. 3 as function of the DMSO concentration together with the dependence calculated from Eq. (1) and with the electrode coverage, θ , calculated from the capacity curves published earlier⁶.

DISCUSSION

The character of the continuous changes in the spectrum of the V(II) complex suggests that the water molecules in the primary ligand sphere are gradually replaced by DMSO molecules. Fig. 2 shows two characteristic intersections of nearly linear portions of the dependences of relative absorbances on the DMSO concentration (for 25.5 and 65.5% DMSO). Hence, it can be assumed that one of the solvated forms prevails in solution at these concentrations. The linear dependence in the particular concentration ranges implies the presence of two prevailing solvate forms

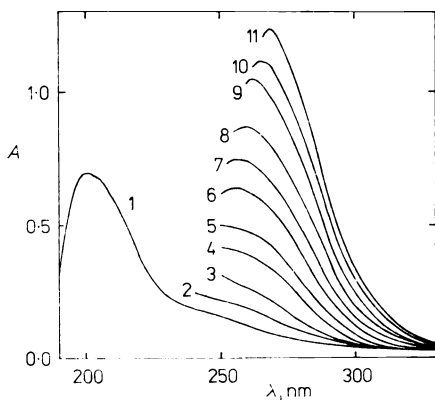


FIG. 1

Spectra of the V(II) complex (conc. $1.25 \text{ mmol dm}^{-3}$) in aqueous DMSO solutions containing 0.5 M HClO_4 . Concentration of DMSO: 1 0; 2 10; 3 20; 4 30; 5 40; 6 50; 7 60; 8 70; 9 80; 10 90; 11 95 per cent

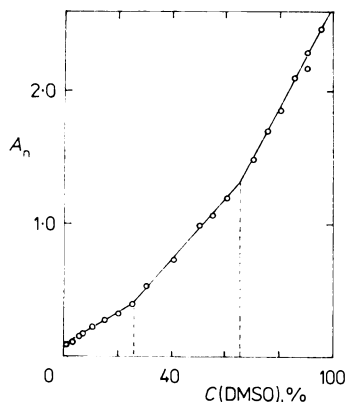


FIG. 2

Dependence of relative absorbance of V(II) on the solution composition (mean value of the ratio of absorbance at 260, 270, 280, and 290 nm to the absorbance of a solution containing 50% DMSO at the same wave length)

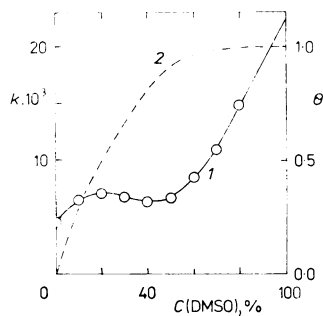


FIG. 3

Dependence of the rate constant for the V(II)/V(III) system on the DMSO concentration. Measured data are indicated by the points, curve 1 was calculated from Eq. (1) by using the data from Table I and those given in the text; curve 2 shows the coverage, θ , as function of the DMSO concentration

with low values of the corresponding equilibrium constants. This is in accord with the results of Kodejš et al.⁹ and Petrella et al.¹⁰, who found that DMSO not only interacts strongly with water molecules but can also replace them in the solvation sphere in proportion to its concentration in solution. This also corresponds to the results of Brown¹¹, who found that DMSO acts as a Lewis base of a similar or somewhat higher strength than water during bonding with metal cations in oxidation states +1 to +3. According to the increasing DMSO concentration, the primary solvation sphere is apparently modified in turn with the formation of solvates having the ratio of H₂O : DMSO equal to 6 : 0, 4 : 2, 2 : 4, and 0 : 6 (further denoted as A, B, C, and D, respectively).

The anomalous dependence of the rate constant of the electrode reaction on the DMSO concentration can be elucidated by assuming different values of the rate constant for the particular solvates on the covered and non-covered electrode surface:

$$k = \sum_X C(X) [k(X, H_2O)(1 - \theta) + k(X, DMSO)\theta]/100, \quad (1)$$

where $k(X, H_2O)$ is the rate constant for solvate X on the water-covered surface, $k(X, DMSO)$ is the rate constant on the DMSO-covered surface, and $C(X)$ is the content of the solvate X in the mixture in per cent. In accord with the linear course of the relative absorbance in Fig. 2, the per cent content of the solvates was calculated from the solvent composition by linear extrapolation.

The constant $k(A, H_2O)$ was measured directly, the constant $k(C, DMSO)$ was taken from the experimental dependence at 65.5% DMSO, in which case the solvate C prevailed in solution and the electrode surface was nearly fully covered with DMSO. The constant $k(D, DMSO)$ was obtained by extrapolating the experimental dependence for 100% DMSO. Therefore, the term with the constant $k(D, H_2O)$ plays no role. The other constants were obtained from experimental data by the least squares method. The results are summarized in Table I and the dependence of the rate constant on the solvent composition is illustrated in Fig. 3.

TABLE I

Rate constants for the system V(II)/V(III) in water-DMSO mixtures

Solvate X	$k(X, H_2O) \cdot 10^3$ cm s ⁻¹	$k(X, DMSO) \cdot 10^3$ cm s ⁻¹
A	4.48	1.00
B	15.71	1.05
C	13.40	9.40
D	—	22.2

From Table I, the following conclusions can be made: Similarly to the acetone–water system¹, the redox reaction for vanadium ions solvated with water proceeds more slowly on the surface covered with the organic component than on the surface covered with water. With increasing DMSO content in the solvation sphere, the rate of the electrode reaction on the surface covered with the organic component increases. With these complexes, solvated with an organic species that is more basic than water, and having a higher content of DMSO in the primary solvation sphere (solvates C and D), the rate of the electrode reaction is higher on the DMSO-covered surface than that of a complex solvated with water on the non-covered surface. Further, it can be seen from Table I that the presence of DMSO in the primary solvation sphere accelerates the electron transfer on the covered surface, which is probably due to a higher polarizability of the solvation sphere through which the electron is transferred. On the other hand, when the electrode surface is only partially covered, the rate of the electrode reaction is higher on the part of the surface that is covered with water than on the part that is covered with the organic. This can be elucidated by the fact that the DMSO monolayer is thicker than the water monolayer. The distance from the electrode surface covered with water, at which V(III) ions are reduced, is hence smaller than that at which these ions are reduced when the surface is covered with DMSO; accordingly, the electrode reaction proceeds at different local ϕ_2 potentials. The influence of the discrete character of the outer Helmholtz plane on electrode reactions was also discussed by Asada¹² and Elliot¹³. On the whole, however, changes of the rate constant do not exceed one order of magnitude, whereas with solvents less basic than water the values of the rate constant in the mean concentration region of the organic component are by up to three orders of magnitude lower. This also suggests that the effects of DMSO and water in the primary solvation sphere are similar.

The results of our measurements are in accord with the values measured by Galus et al.⁴ for the system V(III)/V(II) in aqueous DMF and by Behr et al.³ for the system Eu(III)/Eu(II) in the same solvents; the authors did not consider the possibility of existence of solvates of different composition in discussing the dependence of the rate constants on the concentration of the organic component. The mentioned concept enabled us to describe this dependence in the whole concentration range and to discuss the function of the organic component in the primary solvation sphere of vanadium cations and in the electric double layer.

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