REDUCTION OF THE PERSULFATE ANION IN DIMETHYL SULFOXIDE

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The development of the theory of the elementary event of charge transfer necessitates experimental data on the dependence of the kinetics of the electrode reactions on the structure of the solvent. The most convenient reactions for the establishment of this dependence are the reactions of reduction of certain anions, for example, $S_2O_8^{2-}$, since in the case of negative charges of the surface, there is no specific adsorption of the reacting particle and the reaction product, and the influence of the solvent on the rate of discharging is determined only by the influence on the heat of the elementary event of the process and on the reorientation of the dipoles of the solvent.

Recently the electroreduction of the persulfate anion was investigated on a dropping mercury electrode in formamide [1] and ethylene glycol [2]; moreover, the dependence of the reaction rate on the electrode potential, nature and concentration of the indifferent electrolyte proved analogous to the patterns observed earlier for this reaction in aqueous solutions [3, 4]. The formation of associates of the $NaS_2O_8^-$ type was established in ethylene glycol [2]. The are no data in the literature on the investigation of the mechanism of the reduction of anions in aprotonic solvents.

In view of this, we studied the kinetics of the reduction of the persulfate anion on a dropping mercury electrode in dimethyl sulfoxide (DMSO). The solvent DMSO was redistilled twice under vacuum in the presence of calcium hydride and additionally purified with specially prepared activated charcoal [5]. All the potentials in the work are given relative to an aqueous normal calomel electrode, connected to the cell through a bottle with a saturated solution of KCl in water.

Figure 1 presents the polarization (I versus φ) curves of the electroreduction of 10^{-3} N $Na_2S_2O_8$ on a dropping mercury electrode in DMSO in the presence of $NaClO_4$ in various concentrations. The persulfate anion begins to be reduced at positive charges of the surface; in the region of the zero charge potential there is a sharp inhibition of the reaction rate to values comparable with the points of charging on a dropping mercury electrode in dimethyl sulfoxide. The interval of practically complete inhibition of the reaction is ∿0.8 V. When the cathodic potential ($-\varphi$) is further increased, the rate of discharging of the anion rises

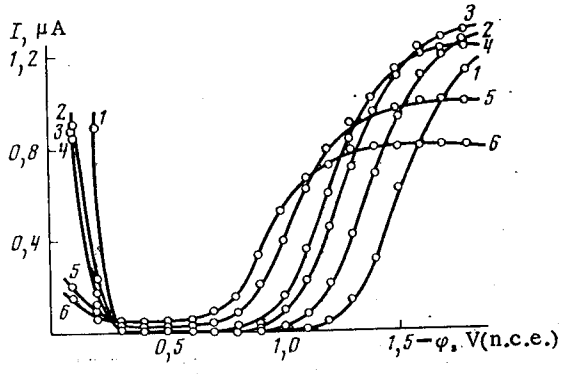

Fig. 1. Polarization curves of the reduction of 10^{-3} N $Na_2S_2O_8$ in DMSO on a dropping mercury electrode in the presence of $NaClO_4$ in concentrations: 1) 10^{-2} N; 2) $2.5\cdot10^{-2}$ N; 3) $5\cdot10^{-2}$ N; 4) 10^{-1} N; 5) $5\cdot10^{-1}$ N; 6) 1 N.

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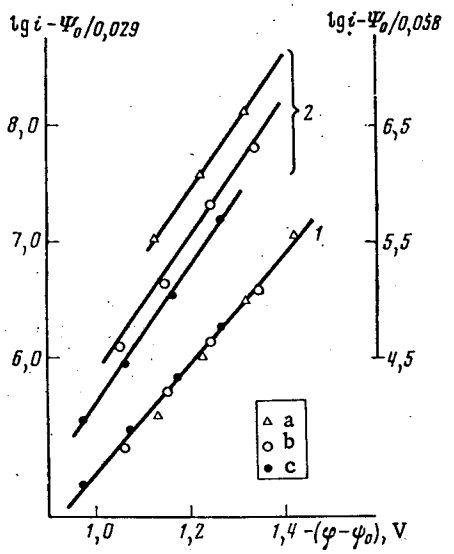

Fig. 2. Corrected Tafel functions of the reduction of 10^{-3} N $Na_2S_2O_8$ in the presence of $NaClO_4$ in a concentration of 10^{-2} N (a), $2.5\cdot10^{-2}$ N (b), $5\cdot10^{-2}$ N (c), calculated with $n_1 = -1$ (1) and with $n_1 = -2$ (2).

(Fig. 1, curve 1). Increasing the $NaClO_4$ concentration leads to an increase in the rate of reduction of $S_2O_8^{2-}$ at negative charges of the surface ($\varepsilon < 0$) and to a decrease in the rate of discharging when $\varepsilon > 0$. At the zero charge potential (ZCP) of mercury in DMSO, equal to -0.315 V, the rate of electroreduction of $S_2O_8^{2-}$ does not depend on the $NaClO_4$ concentration, and all the I versus φ curves intersect at practically the same common point.

The dependence of the rate of reduction of persulfate anions on the electrode potential and concentration of the supporting electrolyte in nonaqueous solvents had not been observed previously in this form. It can be explained on the basis of the theory of electroreduction of anions developed by Frumkin [3, 4], based on the assumption that the elementary event of the electrochemical reaction proceeds at some finite rate, and the rate of discharging i is equal to [4]

$$i = kc_A \exp\left[\frac{\alpha F}{RT}\left(-\varphi + \frac{-n_1+\alpha}{\alpha}\psi_1\right)\right], \quad (1)$$

where k is the rate constant of the reaction, c_A is the volume concentration of the anion, n_1 is the charge of the anion considering the sign, α is the transport coefficient, and ψ_1 is the potential at the point where the discharging particle is situated.

From Eq. (1) it follows that the dependence of log i on φ should be expressed by a curve with a maximum of the current at $\varepsilon > 0$ and with a minimum at $\varepsilon < 0$, while with increasing concentration of the supporting electrolyte, when the absolute value of the ψ_2 potential decreases, the reaction rate at positive charges drops, and at negative charges it rises. At the ZCP, the current density should not depend on the concentration of the supporting electrolyte, and the log i versus φ curves intersect at one common point. A similar dependence is observed in aqueous solutions in the reduction of the persulfate anion with a turbulent system of mixing on an amalgamated copper electrode [4] and in the reduction of the BrO_4^- anion on a dropping mercury electrode [6]. We obtained an intersection of the log i versus φ curves of the reduction of the persulfate anion on a dropping mercury electrode in DMSO at the ZPC in solutions of $NaClO_4$ and KPF_6 of various concentrations. The possibility of observing such a dependence involves a substantially lower rate of discharging the persulfate anion in DMSO in comparison with the rate of discharging of this anion from aqueous solutions.

From data on the dependence of the reaction rate on the concentration of cations of the supporting electrolyte at negative charges of the surface, we calculated the charge of the reacting particle n_1, using the function

$$\left(\frac{\partial \ln i_k}{\partial \ln c}\right)\varphi - \frac{RT}{n_2F}\ln c = -\frac{n_1}{n_2}, \quad (2)$$

derived in [7] (i_k is the kinetic current of the discharging of the anion; n_2 is the charge of the cation of the supporting electrolyte). For the calculation of n_1, the experimental points were corrected according to the theory of nonequilibrium diffusion [8]. The determination was performed for solutions of 10^{-3} N $Na_2S_2O_8$ and 10^{-3} N $K_2S_2O_8$ in the presence of various concentrations of $NaClO_4$ and KPF_6, respetively. When the condition $\varphi - (RT/n_2F)\ln c = \text{const}$ is fulfilled for all potentials, a linear dependence of log i_k on log c is observed, and the average values calculated from the slope are $n_1 = -1.3 \pm 0.02$ in $NaClO_4$ solutions and $n_1 = -1.75 \pm 0.02$ in KPF_6 solutions. The lower than theoretical values of the charge of the persulfate anion indicate the formation of ionic associates in the volume of the solution [9]. This hypothesis is confirmed by the virtual coincidence of the corrected Tafel functions (CTF) for the reduction of $S_2O_8^{2-}$ in the presence of various $NaClO_4$ concentrations under the

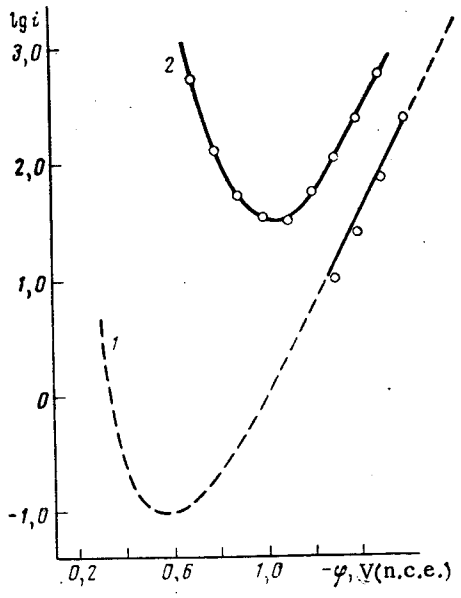

Fig. 3. Dependence of the rate of reduction of the $S_2O_8^{2-}$ anion on the potential of 10^{-3} N $Na_2S_2O_8$ + 10^{-2} N NaF in water (1), 10^{-3} N $Na_2S_2O_8$ + 10^{-2} N $NaClO_4$

condition that in the calculation of the CTF the approximate value $n_1 = -1$ was used (Fig. 2). With a KPF_6 supporting electrolyte, optimum results are obtained on the assumption that $n_1 = -2$. In this case it was assumed that ψ_1 potential is equal to the potential of the external Helmholtz plane (ψ_0), while the charges of the surface needed for the calculation of the ψ_0 potential were found by numerical integration of the curves of the differential capacitance in the corresponding solutions.

If we extrapolate the CTF on the assumption of their linearity to the region of potential where the discharging currents on the I versus φ curves are so low that a calculation of the CTF according to the experimental data is impossible, and then, using the dependence of the ψ_0 potential on the electrode potential, calculate the polarization curves, the dependence of the log i on φ calculated in this way for the discharging of $S_2O_8^{2-}$ in DMSO proves to be similar in form to the dependence of log i on φ in this reaction in aqueous solutions (Fig. 3). However, the rate of the reduction of $S_2O_8^{2-}$ in DMSO is substantially lower than in water. Correspondingly, the heterogeneous rate constants k_s^0 of the reduction of the persulfate anion in solutions of 10^{-3} N $Na_2S_2O_8$ + 10^{-2} N $NaClO_4$ are equal to $5 \cdot 10^{-3}$ cm/sec in aqueous solutions and $6.5 \cdot 10^{-7}$ cm/sec in DMSO.

The existence of a dependence of the rate of electroreduction of the $S_2O_8^{2-}$ anion on the nature of the solvent agrees with the theory of decelerated discharging. This dependence may be partially due to a change in the energy of reorganization of the solvent, a partial overlapping of the wave functions of the initial and final states. However, it should be kept in mind that the value of the equilibrium potential (φ_{eq}) of the system $S_2O_8^{2-}/SO_4^{2-}$ in DMSO is unknown, and the slowdown of $S_2O_8^{2-} + 2\bar{e} \rightarrow 2SO_4^{2-}$ after a change from water to DMSO at a constant overvoltage of the reaction may be associated to some degree with a change in φ_{eq} on account of the lower energy of solvation of the anions in DMSO in comparison with water [10]. Finally, for the system considered in the case of a $NaClO_4$ supporting electrolyte, we should consider the change in the nature of the reacting particle ($S_2O_8^{2-}$ in water and $NaS_2O_8^-$ in DMSO). To evaluate the role of each of the above-mentioned factors in the decrease in the rate of the step of discharging in the case of a change from water to DMSO, an additional investigation will be needed.

The value of ZCP of mercury in DMSO, found in this work, is in good agreement with the results of Payne [11].

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