A STUDY OF THE REDUCTION OF THE MnO_4^- ANION AT A DROPPING MERCURY ELECTRODE

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For a large groups of doubly- and triply-charged anions whose reduction begins at potentials corresponding to positive charges on the electrode surface, retardation of the reaction is observed at potentials more negative than the electrocapillary zero of the electrode. The effect of reaction retardation is due to the influence of the structure of the electrical double layer and has been explained qualitatively and quantitatively on the basis of the theory of retarded discharge [1].

Retardation of the reaction for negative charges on the surface should also have been observed for the case of singly-charged anions. Up to the present time, however, no effect of reaction retardation had been observed for any singly-charged anion whose reduction begins at potentials more positive than the electrocapillary zero of the electrode. N. Konopik [2] observed retardation of the reaction for the reduction of $NaClO_2$ from alkaline solutions but he related the observed effect not to the reduction of ClO_2^- but to the reduction of $HClO_3^{2-}$. G. M. Florianovich and A. N. Frumkin [3] observed a minimum current on the I-φ curve for the reduction of MnO_4^- but attributed the retardation of the reaction to the formation of a film on the mercury drop as a result of its oxidation by potassum permanganate. The aim of the present work was to study the nature of the minimum current and the kinetic relationships for the cathodic reduction of MnO_4^- at a dropping mercury electrode. The studies were carried out by recording the polarization curves (I-φ), by recording curves giving the dependence of the current flowing to the drop on the duration of growth of the drop (I-τ) on a TSLA-01 oscillographic polarograph, and by measuring the differential capacity (c-φ) by means of an alternating current bridge [4]. All the potentials in the present paper are given in volts relative to the normal calomel electrode. We used a capillary with the following characteristics: m = 1.58 mg/sec, τ = 5.0 sec at φ = -1.0. The anode consisted of a platinum plate with an area of 2 cm^2. The salt $KMnO_4$ was recrystallized four times from twice-distilled water. Because of the instability of dilute $KMnO_4$ solutions, the latter were prepared directly before each experiment as follows: a standard solution of 0.1 M $KMnO_4$, prepared by the method described in [5], was diluted with oxygen-free twice-distilled water.

By using this method of preparing the solutions we were able to obtain reproducible data in the study of the reduction of MnO_4^-. It is known from literature data [6] that the reduction of MnO_4^- in neutral solutions takes place in two stages; we studied the first stage: the reduction of MnO_4^- to Mn^{2+}.

In the reduction of $5 \cdot 10^{-4}$ M $KMnO_4$, the I-φ curve shows the drop in current at negative charges on the surface, characteristic of the electrolytic reduction of doubly- and triply-charged anions. The drop in current is observed both when the curve is recorded from less negative and more negative charges on the surface and when the curve is recorded in the opposite sequence (Fig. 1, curve 1).* The retardation of the reaction decreases when foreign cations are introduced into the solution and disappears completely when 0.02 N NaF is added. To determine the nature of the drop in the current during the reduction of MnO_4^-, we recorded the c-φ curves in the presence of $KMnO_4$. If the drop in current on the I-φ curves is associated with the formation of an oxide film, the c-φ curves in the presence of $KMnO_4$ should show a decrease in capacity at potentials corresponding to the retardation of the reaction. The measurements which we carried out showed, however, that the differential capacity in a solution of 10^{-3} N NaF + $5 \cdot 10^{-4}$ M $KMnO_4$ coincides, within the limits of experimental error, with the capacity measured in 10^{-3} N NaF solution.

The formation of an oxide film on the surface of the drop should lead to a decrease in the MnO_4^- reduction current flowing to the drop during its growth [7]. The I-τ curves show no decrease in current, however, indicating the

* Figures 1 and 2 give only the sections of the polarization curves which are not distorted by polarographic maxima of the first type.

absence of oxide film on the electrode surface. At potentials corresponding to the limiting diffusion current, the dependence of I on τ for the reduction of MnO_4^- was determined by diffusion, and the current $I = k\tau^{1/5}$. At the potentials of the minimum current, the dependence of the current on the duration of growth of the drop in the reduction of MnO_4^- is described by the equation $I = k\tau^{1/3}$. The fact that the power of the function is different from that obtained for the reduction of other anions ($I = k\tau^{2/3}$) is related to the fact that, in the case of the reduction of the singly-charged MnO_4^-, the concentration polarization at the minimum on the $I-\varphi$ curve under the given capillary operating conditions was much greater than that for the reduction of $S_2O_8^{2-}$. As in the case of the reduction of other anions, the retardation of the reaction disappears when organic cations are added to the solution, the effect of their action increasing with increase in the concentration of the organic cation and also with increase in the length of the organic chain (Fig. 2) [8].

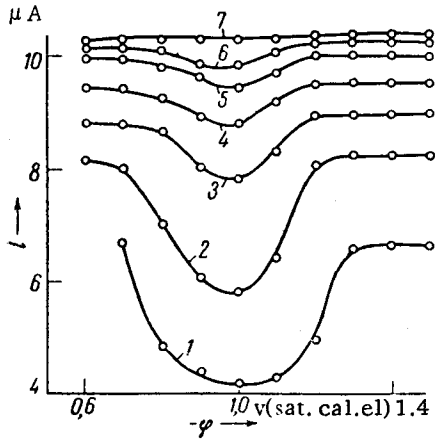

Fig. 1. Polarization curves for the reduction of $5 \cdot 10^{-4}$ M $KMnO_4$ in the presence of NaF in concentrations of: 1) 0; 2) 10^{-3} N; 3) $2 \cdot 10^{-3}$ N; 4) $3 \cdot 10^{-3}$ N; 5) $5 \cdot 10^{-3}$ N; 6) $7.5 \cdot 10^{-3}$ N; 7) $2 \cdot 10^{-2}$ N.

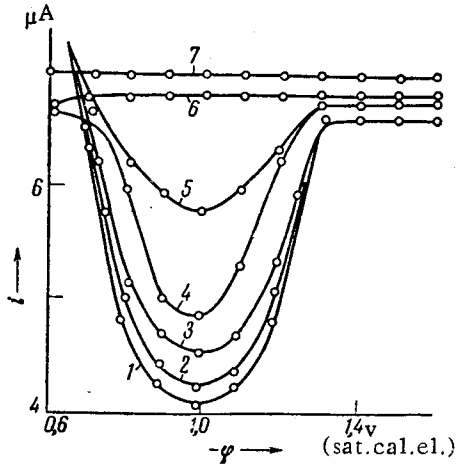

Fig. 2. Polarization curves for the reduction of $5 \cdot 10^{-4}$ M $KMnO_4$ in the presence of the following additives: $[(C_4H_9)_4N]_2 \cdot SO_4$: 1) 0; 2) $3.8 \cdot 10^{-6}$N; 3) 10^{-5}N; 4) $1.5 \cdot 10^{-5}$N; $[(C_2H_5)_4N]_2\,SO_4$; 5) 10^{-5}N; 6) $3.0 \cdot 10^{-5}$N; 7) 10^{-4}N.

It follows from the above experimental data that the drop in current on the $I-\varphi$ curves for the reduction of MnO_4^- is of the same nature as the current drops observed in the reduction of doubly- and triply-charged anions and that the kinetics of the reduction of MnO_4^- should be described by the equation of the theory of retarded discharge. As Frumkin and Petrii [9] have shown, the applicability of the theory of retarded discharge to a given reaction can be confirmed by determining the charge of the particle being reduced, from the dependence of the rate of reduction on the concentration of the cations of the supporting electrolyte. If the adsorption of all the anions of the solution Γ_a at negative charges on the surface is small compared with the adsorption of cations Γ_c and the condition of invariance of charge [7] is observed, we have

$$\left(\frac{\partial \ln i}{\partial \ln C}\right)_{\varphi} = \frac{RT}{n_2 F} \ln C = -\frac{n_1}{n_2}, \qquad (1)$$

where i is the kinetic current for reduction of the anion, C the total concentration of the cations of the supporting electrolyte, n_1 the charge of the reacting particle, and n_2 the charge of the cations of the supporting electrolyte.

We studied the reduction of $5 \cdot 10^{-4}$ M $KMnO_4$ in the presence of different concentrations of NaF, KF, and CsF (Fig. 1). The retardation effect is removed when these salts are added. The increase in the limiting current with increase in the concentration of indifferent electrolyte is attributed to the removal of the migration effect and this is confirmed by the fact that the value of the limiting current in the presence of 0.1 N NaF agrees with the diffusion current calculated from the Ilkovic equation. The dependence of the rate of reduction of MnO_4^- on the activity of the cation of the supporting electrolyte in KF solutions is shown in Fig. 3. Calculation of n_1 from these data gives $n_1 = -0.9$ at $\varphi = -0.9$ and $n_1 = -1.1$ at $\varphi = -1.0$, which show good agreement with the theoretical value of $n_1 = -1.0$. The transfer coefficient α can be determined from the experimental data for the relationship $I = f(\varphi)$. For this purpose, however, it is necessary to know the value of the ψ_1-potentials for solutions of the supporting electrolyte. The values of the ψ_1-potentials for NaF were calculated from the charges given in [10], in the calculation of the ψ_1-

potentials in CsF solutions the values of the charges were taken from [11], and for KF we used the charges determined in KCl solutions [11]. In the determination of α the experimental data were plotted on coordinates

$$\left(\lg i + \frac{n_1\psi_1 F}{2{,}3RT}\right) - (\varphi - \psi_1)$$

(corrected Tafel relationships – c.t.r.) and are represented in Fig. 4. The value of α was found from the slope of the linear section of the c.t.r. in these coordinates. It can be seen from Fig. 4 that for MnO_4^- in the presence of NaF, KF, and CsF, the slopes of the curves are the same and equal to $\alpha \simeq 0.2$. The rate of reduction of MnO_4^- increases on going from Na^+ to Cs^+, as is observed in the reduction of other anions.

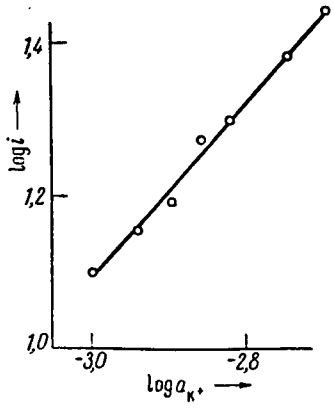

Fig. 3. Dependence of the rate of reduction of $5 \cdot 10^{-4}$ M $KMnO_4$ on the activity of KF (at $\varphi = -1.0$ in a solution containing $5 \cdot 10^{-4}$ N KF).

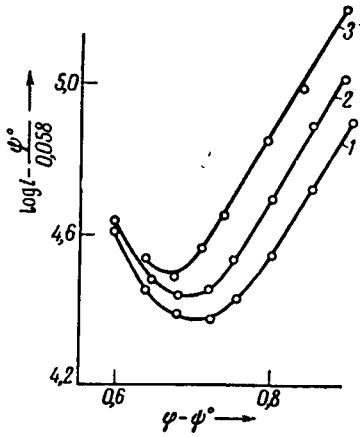

Fig. 4. Corrected Tafel relationships for the reduction of $5 \cdot 10^{-4}$ M $KMnO_4$ in the presence of: 1) 10^{-3} N NaF; 2) 10^{-3} N KF; 3) 10^{-3} N CsF.

At potentials close to the electrocapillary zero of mercury, the c.t.r. show a minimum which, unlike the case of the reduction of $S_2O_8^{2-}$ [12], is more clearly defined and is observed for all singly-charged cations of the supporting electrolyte. This is apparently related both to the smaller effect of the ψ_1-potential on the reduction of singly-charged anions [1] and to the possible specific adsorption of MnO_4^- on mercury. Justification for this suggestion is provided by the marked adsorption of the MnO_4^- anion at a solution/air boundary [13].

Thus, the study of the reduction of MnO_4^- has shown that the reduction of singly-charged anions involves reaction retardation, whose nature is analogous to the retardation of the reaction for multi-charged anions and is associated with the influence of the structure of the electrical double-layer on the kinetics of the electrode processes.

In conclusion we wish to thank Academician A. N. Frumkin for consultation and interest in the work.

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