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

(Presented by Academician A. N. Frumkin, 13 V 1963)

For a large group of doubly and triply charged anions whose reduction begins at potentials corresponding to positive charges of the electrode surface, inhibition of the reaction is observed at potentials more negative than the point of zero charge of the electrode. The effect of reaction inhibition is due to the influence of the structure of the electrical double layer and has received a qualitative and quantitative explanation on the basis of the theory of delayed discharge ([1]).

Reaction inhibition at negative surface charges should also be observed in the case of singly charged anions. However, up to the present, for no singly charged anion whose reduction begins at potentials more positive than the point of zero charge of the electrode has an effect of reaction inhibition been observed. H. Konopik ([2]), in the reduction of $NaClO_2$ from alkaline solutions, observed reaction inhibition, but associated the observed effect not with the reduction reaction of ClO_2^-, but with the reduction of $HClO_3^{2-}$. G. M. Florianovich and A. N. Frumkin ([3]), in the reduction of MnO_4^-, observed a current minimum on the I–φ curve, but explained the reaction inhibition by the formation of a film on the mercury drop as a result of its oxidation by potassium permanganate. The aim of the present work was to study the nature of the current minimum and the kinetic regularities of the cathodic reduction of MnO_4^- at a mercury dropping electrode. The investigation was carried out by recording polarization curves (I–φ), by recording curves of the dependence of the current flowing to the drop on the time of drop growth (I–τ) on a TsLA-01 oscillographic polarograph, and by measuring the differential capacitance (c–φ) with the aid of an alternating-current bridge ([4]). All potentials in the work are given in volts relative to the normal calomel electrode. In the work a capillary with the following characteristics was used: $m = 1.58$ mg/sec, $\tau = 5.0$ sec at $\varphi = -1.0$ V. A platinum plate of area 2 cm^2 was used as the anode. The $KMnO_4$ salt was recrystallized four times from bidistillate. Because of the instability of dilute

Figure 1 and Figure 2: polarization curves

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$KMnO_4$ solutions, the latter were prepared immediately before each experiment by dilution with bidistillate, freed from oxygen, of a standard 0.1 M $KMnO_4$ solution prepared according to the procedure described in (^{5}).

The use of the indicated procedure for preparing solutions made it possible for us to obtain reproducible data in studying the reduction of MnO_4^-. From literature data (^{6}) it is known that the reduction of MnO_4^- in neutral solutions proceeds in two stages; we studied the first stage: reduction of MnO_4^- to Mn^{+2}.

In the reduction of $5 \cdot 10^{-4}$ M $KMnO_4$, a decrease in current is observed on the I —φ curve at negative surface charges, characteristic of electroreduction reactions of doubly and triply charged anions. The decrease in current is observed both when recording the curve from less negative to more negative surface charges and in the reverse sequence (Fig. 1,

curve 1)*. The inhibition of the reaction decreases when foreign cations are introduced into the solution and disappears completely upon addition of 0.02 N NaF. To clarify the nature of the current decrease during the reduction of MnO_4^-, c—φ curves were recorded in the presence of $KMnO_4$. If the appearance of a current decrease on the I—φ curves is associated with the formation of an oxide film, then on the c—φ curves, in the presence of

Fig. 1. Polarization curves for the reduction of $5 \cdot 10^{-4} M$ $KMnO_4$ in the presence of NaF at concentrations:
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 additives: $[(C_4H_9)_4N]_2 \cdot SO_4$:
1—0, 2—$3.8 \cdot 10^{-6} N$, 3—$10^{-5} N$, 4—$1.5 \cdot 10^{-5} N$;
$[(C_2H_5)_4N]_2SO_4$, 5—$10^{-5} N$, 6—$3.0 \cdot 10^{-5} N$, 7—$10^{-4} N$.

$KMnO_4$, at potentials corresponding to inhibition of the reaction, a decrease in capacitance should be observed. However, the measurements carried out showed that the differential capacitance in a solution of 10^{-3} N NaF + $5 \cdot 10^{-4}$ M $KMnO_4$ coincides, within experimental error, with the capacitance measured in a 10^{-3} N NaF solution.

Formation of an oxide film on the surface of the drop should lead to a decrease in the reduction current of MnO_4^- flowing to the drop during its growth $^{(7)}$. But on the I—τ curves no decrease in current is observed, which indicates the absence of an oxide film on the electrode surface. At potentials corresponding to the limiting diffusion current, the dependence of I on τ during reduction of MnO_4^- was determined by diffusion, and the current $I = k\tau^{1/6}$. At potentials of the current minimum, the dependence of the current on the growth time of

Figure 3 and Figure 4: graphs

Figure 2: Figure 3 and Figure 4: graphs

the drop during reduction of MnO_4^- is described by the equation $I_i = k\tau^{1/3}$. A different power-law dependence from that obtained in the case of reduction of other anions ($I = k\tau^{2/3}$) is due to the fact that, in the case of reduction of singly charged MnO_4^-, at the minimum of the i–φ curve under the given operating regime of the capillary, the concentration polarization was considerably greater than in the case of reduction of $S_2O_8^{2-}$. As in the case of reduction of other anions, the inhibition of the reaction is removed when organic cations are introduced into the solution, and the effect of their action increases both with increasing concentration of the organic cation and with increasing length of the organic chain (Fig. 2) (8).

From the experimental data presented it follows that the current decrease on the I–φ curves for the reduction of MnO_4^- has the same nature as the observed current decreases during the reduction of di- and trivalent anions, and the kinetics of the reduction reaction of MnO_4^- should be described by the equation of the theory of delayed discharge. As Frumkin and Petrii (9) showed, the applicability of the theory of delayed discharge to a given reaction can be checked by determining, from the dependence of the reduction rate on the concentration of the supporting cations, the charge of the particle being reduced. If the adsorption of all solution anions Γ_a at negative surface charges is small in comparison with the adsorption of cations Γ_k, and the condition of charge invariance (7) is satisfied, then

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

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

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 with addition of $5 \cdot 10^{-4} N$ KF)

Fig. 4. Corrected Tafel dependences of 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

We studied the reduction of $5 \cdot 10^{-4} M$ $KMnO_4$ in the presence of various concentrations of NaF, KF, and CsF (Fig. 1). Upon introduction of these salts,

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* In Figs. 1 and 2 only those portions of the polarization curves are shown which are not distorted by polarographic maxima of the first kind.

the inhibiting effect is removed. The increase in limiting current with increasing concentration of indifferent electrolyte is explained by the removal of the migration effect, which is confirmed by the agreement of the limiting current in the presence of $0.1N$ NaF with the diffusion current calculated from the Ilkovič equation. Figure 3 shows the dependence of the rate of the reduction reaction of MnO_4^- on the activity of the supporting cation in KF solutions. Calculations of n_1 from these data give, at $\varphi = -0.9$, $n_1 = -0.9$, and at $\varphi = -1.0$, $n_1 = -1.1$, which agrees well with the theoretical value $n_1 = -1.0$. From the experimental data for the dependence $I = f(\varphi)$, the transfer coefficient α can be determined. However, for this it is necessary to know the values of the ψ_1-potentials for the supporting solutions. The values of the ψ_1-potentials for NaF were calculated from the charges given in ([10]); for calculating the ψ_1-potentials in CsF solutions, the charge values were taken from ([11]); for KF, charges determined in KCl solutions ([11]) were used. To determine α, the experimental data were represented in the coordinates

$$\left(\lg i + \frac{n_1 \psi_1 F}{2.3RT}\right) - (\varphi - \psi_1)$$

(corrected Tafel dependences —c.t.d.) and are shown in Fig. 4. From the slope of the linear part of the c.t.d. in these coordinates, α was found. As can be seen from Fig. 4, for MnO_4^- in the presence of NaF, KF, and CsF, the slope of the curves

is the same and equal to $a \simeq 0.2$. The rate of reduction of MnO_4^- increases in going from Na^+ to Cs^+, as is also observed in the reduction of other anions.

At potentials close to the potential of the point of zero charge of mercury in i. t. z., a minimum appears which, in contrast to the reduction reaction of $S_2O_8^{2-}$ ([12]), is more pronounced and is observed for all singly charged cations of the supporting electrolyte. This apparently is connected both with the smaller effect of the ψ_1-potential on the reduction of singly charged anions ([1]), and with possible specific adsorption of MnO_4^- on mercury. The basis for such an assumption is the large adsorption of the MnO_4^- anion at the solution/air interface ([13]).

Thus, the study of the reduction of MnO_4^- has shown that, in the reduction of singly charged anions, inhibition of the reaction is observed; the nature of this inhibition is analogous to the inhibition of the reaction for multicharged anions and is associated with the influence of the structure of the electrical double layer on the kinetics of electrode processes.

In conclusion, we consider it our pleasant duty to express our gratitude to Academician A. N. Frumkin for his constant consultation and attention to the work.

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