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O. A. PETRII, Academician A. N. FRUMKIN

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Abstract

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O. A. PETRII, Academician A. N. FRUMKIN

ON THE DETERMINATION OF THE CONSTANT α FROM THE DEPENDENCE OF THE KINETICS OF ELECTROREDUCTION ON POTENTIAL AND SUPPORTING-ELECTROLYTE CONCENTRATION

In paper ([1]) a rigorous method was proposed for determining the charge of the reacting particle from the dependence of the process kinetics on the potential and the concentration of the supporting electrolyte. In contrast to the determination of the charge, the determination from experimental data of the transfer coefficient α can in many cases be carried out only approximately, since it requires knowledge of the dependence of ψ_1 on φ and c of the supporting electrolyte (here and below the notation is the same as in paper ([1])) and, consequently, depends on the assumed picture of the structure of the double layer and on assumptions about the position of the center of the particle in the transition state near the interface.

For determining α it is convenient to use the relation following from the Frumkin –Florianovich equation ([2]):

$$\lg i + \frac{n_1\psi_1 F}{2.3RT} = \text{const} - \frac{\alpha F}{2.3RT}(\varphi - \psi_1), \tag{1}$$

and to represent the experimental data in the coordinates $\left(\lg i + \frac{n_1\psi_1 F}{2.3RT}\right)$, $(\varphi - \psi_1)$.

An analogous procedure was used in the work of Delahay et al. ([3]). Straight lines in these coordinates with slope $\frac{\alpha F}{2.3RT}$ were called corrected Tafel dependences (c.t.d.) in ([3]).

Let us first assume that the center of charge in the transition state is localized on the outer Helmholtz plane (P_Γ) and that $\psi_1 = \psi_0$. We shall denote the value of

the transfer coefficient obtained under these assumptions by α_0. To calculate the ψ_0 potentials we used ε, φ curves in 10^{-1} and 10^{-2} N NaF according to ([4]) and in 1 N, 10^{-1} N, and 10^{-2} N LiCl, KCl, and CsCl according to ([5]). For solutions of other concentrations the ε, φ curves were found from the experimental curves using the condition of invariance of ε at $\varphi - \dfrac{RT}{n_2 F} \ln a_{\pm} = \text{const}$. The potentials are given in volts relative to the normal calomel electrode.

Determination of α_0 from the slope of the corrected Tafel straight lines for the reduction of H_3O^+, calculated from the data of works ([6]) and ([7]), gives the value 0.50 ± 0.02 in LiCl, KCl, and CsCl supporting electrolytes. The c.t.d. for different supporting-electrolyte concentrations practically coincide with one another.

Figure 1 gives c.t.d. for the reduction of $S_2O_8^{2-}$ on a dropping mercury electrode in LiCl + NaCl, NaF, KCl, and CsCl supporting electrolytes of different concentrations. Concentration polarization was allowed for according to the Meiman –Bagotskii theory ([8]). For different cations the c.t.d. lie in the same sequence as the curves $\lg i(\varphi)$ at equal concentrations of alkali-metal salts. For different concentrations of one and the same cation the c.t.d. coincide completely or approximately. This is fulfilled best for the reduction of $S_2O_8^{2-}$ in CsCl and KCl supporting electrolytes and less well in LiCl, for which the curves, as a rule, lie the lower, the higher the concentration of the supporting electrolyte. The agreement improves as $-(\varphi - \psi_0)$ increases. From equation (6) of paper ([1]), which was obtained on the basis of the thermodynamic theory of electrocapillarity, taking into account that the values of ψ_0 calculated from the theory of the diffuse layer at sufficiently negative φ satisfy the condition $\psi_0 = \text{const} + \dfrac{RT}{n_2 F} \ln c$

at $\varphi - \psi_0 = \text{const}$, one can obtain

$$\left.\frac{\partial \left(\ln i + \frac{n_1 F}{RT}\psi_0\right)}{\partial \ln c}\right|_{\varphi-\psi_0} = 0,$$

whence

$$\ln i + \frac{n_1 F \psi_0}{RT} = f(\varphi - \psi_0).$$

Thus, the coincidence of the i.t.c. obtained at different c must hold over the entire range of applicability of equation (6) of work ([1]), i.e., at sufficiently low c and large $-\varphi$, independently of assumptions about the detailed mechanism of the process and the structure of the double layer. The situation is different with the shape and slope of the i.t.c. At strongly negative φ, the i.t.c. in the solutions studied are rectilinear, and the value α_0, determined from the slope of the straight lines, is 0.30 ± 0.02, in good agreement with that found

by another method in ([2]). However, an almost rectilinear course of the i.t.c. over the whole investigated interval of φ is observed only for the reduction of $S_2O_8^{2-}$ in a CsCl supporting electrolyte. In KCl, NaF, and LiCl supporting electrolytes, a deviation from rectilinearity is observed on approaching the p.z.c., which increases on going from K^+ to Li^+. In the case of NaF and especially LiCl, a minimum is retained on the corrected curves.

Fig. 1. Corrected Tafel curves for the electroreduction of the anion $S_2O_8^{2-}$ in solutions:
a—$10^{-3}N$ $Na_2S_2O_8$ in the presence of LiCl + NaCl ($[Li^+] : [Na^+] = 10 : 1$) at concentrations $10^{-2}N$ (1), $1.5 \cdot 10^{-2}N$ (2), $2 \cdot 10^{-2}N$ (3), $3 \cdot 10^{-2}N$ (4), $4 \cdot 10^{-2}N$ (5), $5 \cdot 10^{-2}N$ (6), $7 \cdot 10^{-2}N$ (7);
b—$10^{-3}N$ $Na_2S_2O_8$ in the presence of NaF at concentrations $3 \cdot 10^{-3}N$ (1), $5 \cdot 10^{-3}N$ (2), $7 \cdot 10^{-3}N$ (3), $10^{-2}N$ (4), $1.5 \cdot 10^{-2}N$ (5), $2 \cdot 10^{-2}N$ (6), $3 \cdot 10^{-2}N$ (7);
c—$10^{-3}N$ $K_2S_2O_8$ in the presence of KCl at concentrations $2 \cdot 10^{-3}N$ (1), $3 \cdot 10^{-3}N$ (2), $4 \cdot 10^{-3}N$ (3), $5 \cdot 10^{-3}N$ (4), $6 \cdot 10^{-3}N$ (5), $7 \cdot 10^{-3}N$ (6), $8 \cdot 10^{-3}N$ (7), $10^{-2}N$ (8);
d—$10^{-3}N$ $Cs_2S_2O_8$ in the presence of CsCl at concentrations 0 (1), $5 \cdot 10^{-4}N$ (2), $10^{-3}N$ (3), $1.5 \cdot 10^{-3}N$ (4), $2 \cdot 10^{-3}N$ (5), $2.5 \cdot 10^{-3}N$ (6), $3 \cdot 10^{-3}N$ (7), $4 \cdot 10^{-3}N$ (8), $5 \cdot 10^{-3}N$ (9).

Unlike the process of discharge of $S_2O_8^{2-}$ considered above, the i.t.c. for the reduction of $Fe(CN)_6^{3-}$ on mercury are convex toward the potential axis. The slope of the rectilinear portions of the curves in the region of large $-\varphi$ gives $\alpha_0 = 0.16$ in a LiCl supporting electrolyte (in agreement with the value obtained earlier in ([8])), 0.17 in a KCl supporting electrolyte, and 0.19 in a CsCl supporting electrolyte. In the initial portion, the i.t.c. in a CsCl supporting electrolyte also have a steeper slope than in the other cases.

If one assumes, as is done in deriving equation (1), that allowance for ψ_0 makes it possible, in principle, to represent correctly the dependence of the effective concentration of the anion on the potential and on the bulk concentration, and that for the reaction of anion reduction, at constant effective concentration of anions, the Tafel equation must be fulfilled, then one may consider the causes of the observed deviations of the i.t.c. from rectilinearity. A possible cause for the appearance of a minimum on the i.t.c. may be slight specific adsor-

tion of $O_2S_8^{2-}$, which leads to higher rates of the process near the p.z.c. than could be expected on the basis of purely electrostatic concepts. Another factor not taken into account in deriving equation (1) is the discrete structure of the double layer. Probably, in a first rough approximation it can be allowed for by considering separately the interaction of the anion with the nearest cation, leading to the formation of a certain analogue of an ion pair in the double layer, while retaining, in order to take account of the action of the other cations, the calculation of ψ_0 according to the classical theory. As follows from the position of the p.z.c., the interaction with the nearest cation decreases in the sequence

Figure 2

Figure 1: Figure 2

$$Cs^+ > K^+ > Na^+ > Li^+.$$

The approximation of the p.z.c. to rectilinearity in the case of CsCl can be explained as the result of mutual compensation of two effects: a decrease in the amount of specifically adsorbed $S_2O_8^{2-}$ with an increase in $-\varepsilon$, and the accompanying increase in the concentration of Cs^+. The role of the latter factor decreases in the series

$$Cs^+ > K^+ > Na^+ > Li^+.$$

This factor determines the form of the p.z.c. for the reduction of $Fe(CN)_6^{3-}$, which is not specifically adsorbed and carries a high negative charge.

Fig. 2. Graphical analysis of the reduction curves of $10^{-3}N$ $Na_2S_2O_8$ in the presence of NaF at concentrations: 1–$3 \cdot 10^{-3}N$, 2–$5 \cdot 10^{-3}N$, 3–$7 \cdot 10^{-3}N$, 4–$10^{-2}N$, 5–$1.5 \cdot 10^{-2}N$, 6–$2 \cdot 10^{-2}N$, 7–$3 \cdot 10^{-2}N$.

The value of a_0 in the reduction of $S_2O_8^{2-}$ was also determined by other methods, which led to results consistent with the conclusions from Fig. 1. Figure 2 shows the determination of a_0 by Hirst' s graphical method ([9]). The curves a connect points corresponding to the condition $\psi_0 = \text{const}$. As follows from equation (1), the slope of these curves

$$\left(\frac{\partial \lg i}{\partial \varphi}\right)_{\psi_0} = -\frac{a_0 F}{2.3RT}$$

does not depend on n_1. In the initial portion the curves a' and a'' have a small negative slope, and only the straight line a''' in the region of large φ gives $a_0 = 0.30$. The curve MN in the lower part of Fig. 2 represents the dependence $\psi_0 - \varphi$ at $\lg i = \text{const}$. At large φ the curve has a rectilinear segment, whose slope

$$\left(\frac{\partial \psi_0}{\partial \varphi}\right)_{\lg i} = \frac{a_0}{n_1 + a_0}$$

for $n_1 = -2$ also gives $a_0 = 0.30$.

We determined the dependence of the rate of reduction of $S_2O_8^{2-}$ at $\varphi = \text{const}$ on $\dfrac{\psi_0 F}{2.3RT}$ in a NaF supporting electrolyte; it is expressed by straight lines with slopes 1.6 at −0.75 V, 1.8 at −0.9 V, 1.85 at −1.1 V, 2.0 at −1.3 V, 2.2 at −1.5

Fig. 3

Figure 2: Fig. 3

V, and 2.3 at −1.6 V. If equation (1) is fulfilled, this slope is equal to $(a_0 - n_1)$. The results we obtained disagree with Hirst' s conclusions ([9]).

Let us now consider the assumption according to which the charge center of the transition state is located at some constant distance x from P_Γ.

in the diffuse part of the double layer. In Fig. 3 the rate-potential curves are given for the reduction of $10^{-3}N$ $Cs_2S_2O_8$ in the presence of $2 \cdot 10^{-3}N$ CsCl, calculated on this assumption for various x. The corresponding values of ψ_x were found from the Gouy theory. When the center of the reacting particle is displaced from P_Γ into the bulk of the solution, there is at first a gradual decrease in the slope of the rate-potential curves. However, down to a distance of ~ 0.6 Å the change in slope is small and still lies within the experimental error. Subsequently, along with the decrease in slope, curvature of the rate-potential curves occurs. Thus, if it is assumed that the constant α reflects some real regularity, it is necessary to exclude the assumption of distances between the center of charge and P_Γ exceeding $\sim$ 3-4 Å in the case of $S_2O_8^{2-}$. The rate-potential curves for the reduction of $Fe(CN)_6^{3-}$ can be straightened if it is assumed that the reaction proceeds at a distance of ~ 10 Å from P_Γ. Since this gives an implausibly small value, $\alpha \simeq 0.05$, further investigation is required to clarify the physical meaning of the result obtained.

Fig. 3. Dependence of the reduction rate of $10^{-3}N$ $Cs_2S_2O_8$ in the presence of $2 \cdot 10^{-3}N$ CsCl on potential (0) and corrected theoretical curves calculated on the assumption that the center of the particle in the transition state is located at distances of 55.4 Å (1), 11.08 Å (2), 5.54 Å (3), 1.108 Å (4), 0.554 Å (5) from the outer Helmholtz plane, and on the outer Helmholtz plane (6).

If it is assumed that the center of the particle in the transition state is localized in the inner part of the double layer, then, as was shown in ([10]), a relation may be obtained between α_0 and the true value of α:

$$\alpha_0 = \alpha + \lambda(n_1 - \alpha), \tag{2}$$

where λ is the ratio of the distance between the center of charge in the transition state and P_Γ to the thickness of the compact part of the double layer. From Eq. (4) it follows that the rate-potential curve should remain rectilinear at $\lambda > 0$, if it is rectilinear at $\lambda = 0$. However, the slope of the rate-potential curve should decrease in the case of cations and increase in the case of anions. Thus, at $n_1 = 1$, $\alpha_0 = 0.50$, and $\lambda = 0.50$, the value of α is 0.25. At $\lambda = 0.08$, $n_1 = -2$, and $\alpha_0 = 0.30$, the value of α proves to be 0.50; and at $n_1 = -3$ and $\alpha_0 = 0.16$, the value $\alpha = 0.50$ can be obtained at $\lambda = 0.097$. Thus, the determination of α

depends to a high degree on the assumptions about the position of the center of charge of the transition state in the compact layer.

Moscow State University
named after M. V. Lomonosov
Institute of Electrochemistry, Academy of Sciences of the USSR

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Note: Figure translations are in progress. See original paper for figures.