DETERMINATION OF THE CONSTANT α FROM THE RELATION OF ELECTROREDUCTION KINETICS TO THE POTENTIAL AND BASE ELECTROLYTE CONCENTRATION

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In [1], a strict method was proposed for determining the charge of a reacting particle from the relation of the kinetics of the process to the potential and base electrolyte concentration. In contrast to the charge, the transport number α may be determined from experimental data only approximately in many cases, as a knowledge of the relation of ψ_1 to φ and $\underline{c}$ of the base electrolyte (the same symbols are used as in [1]) is required and, consequently, the determination depends on the picture adopted for the structure of the double layer and the assumptions on the position of the center of the particle in the transition state close to the interphase.

For the determination of α it is convenient to use the relation derived 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 plot the experimental data in the coordinates $\left(\lg i + \frac{n_1\psi_1 F}{2{,}3RT}\right)$, $(\varphi - \psi_1)$. An analogous method was used in the work of Delahay et al. [3]. In [3], lines in these coordinates with a slope $\frac{\alpha F}{2.3RT}$ were called corrected Tafel relations (c.t.r.).

We will assume first that the center of the charge in the transition state is localized in the outer Helmholtz layer (L_H) and $\psi_1 = \psi_0$. The transport number obtained with these assumptions will be denoted by α_0. To calculate the ψ_0-potentials, we used curves of ε against φ for 10^{-1} and 10^{-2} N NaF from [4], and for 1 N, 10^{-1} N, and 10^{-2} N LiCl, KCl, and CsCl from [5]. For solutions of other concentrations, curves of ε against φ were found from the experimental curve, using the condition that ε is invariant when $\varphi - \frac{RT}{n_2F}\ln a_\pm = \text{const}$. The potentials are given in volts relative to a saturated calomel electrode.

The calculation of α_0 from the slope of corrected Tafel lines for the reduction of H_3O^+, calculated from the data in [6] and [7], leads to the value 0.50 ± 0.02 with LiCl, KCl, and CsCl as the base electrolyte. The corrected Tafel relations for different concentrations of the base electrolyte practically coincided.

Figure 1 gives corrected Tafel relations for the reduction of $S_2O_8^{2-}$ on a mercury dropping electrode in a base electrolyte of LiCl + NaCl, NaF, KCl, and CsCl at various concentrations. Allowance was made for concentration polarization in accordance with the Meiman – Bagotskii theory [8]. For the different cations, the corrected Tafel relations lay in the same sequence as curves of $\log i(\varphi)$ for the same concentrations of alkali metal salts. For different concentrations of the same cation, the corrected Tafel relations completely or approximately coincided. This was most true of the reduction of $S_2O_8^{2-}$ when the base electrolyte was CsCl and KCl, and less so with LiCl, for which the curves generally lay at a lower level, the higher the concentration of the base electrolyte. The agreement improved with an increase in $-(\varphi - \psi_0)$. From Eq. (6) in [1], which was obtained on the basis of the thermodynamic theory of electrocapillarity, taking into account the fact that the values of ψ_0 calculated from the theory of a diffuse layer at sufficiently negative values of φ satisfy the condition $\psi_0 = \text{const} + \frac{RT}{n_2F}\ln c$ with

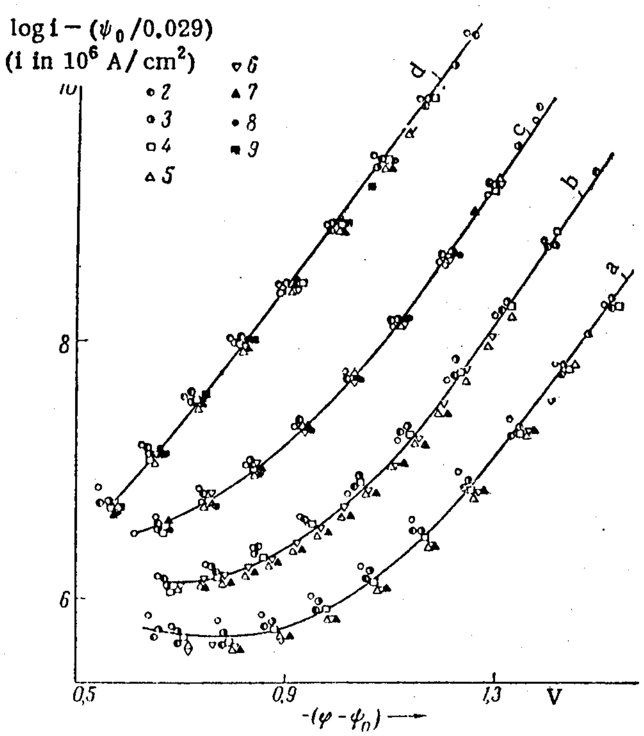

Fig. 1. Corrected Tafel curves of the electroreduction of the anion $S_2O_8^{2-}$ in the following solutions: a) 10^{-3} N $Na_2S_2O_8$ in the presence of LiCl + NaCl $[Li^+]:[Na^+] = 10$; 1) in concentrations 10^{-2} N (1); $1.5 \cdot 10^{-2}$ N (2); $2 \cdot 10^{-2}$ N (3); $3 \cdot 10^{-2}$ N (4); $4 \cdot 10^{-2}$ 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 of $3 \cdot 10^{-3}$ 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); $2 \cdot 10^{-3}$ N (6); $3 \cdot 10^{-3}$ N (7). c) 10^{-3} N $K_2S_2O_8$ in the presence of KCl at concentrations of $2 \cdot 10^{-3}$ 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 of 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).

$\varphi - \psi_0$ = const, it is possible to obtain

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

$= f(\varphi - \psi_0)$. Thus, the corrected Tafel relations obtained at different values of c should coincide in the whole region of applicability of Eq. (6) from [1], i.e., at sufficiently low values of c and high values of φ, regardless of the assumptions on the detailed mechanism of the process and the structure of the double layer. The situation is different with the form and slope of the corrected Tafel relations. With strongly negative values of φ, the corrected Tafel relations for the solutions investigated are linear and the value of α_0 determined from the slope of the lines is 0.30 ± 0.02, which agrees well with the value found by another method in [2]. However, the corrected Tafel relations are almost linear over the whole range of values of φ investigated only in the reduction of $S_2O_8^{2-}$ in a base electrolyte of CsCl. With KCl, NaF, and LiCl as the base electrolytes, a deviation from linearity is observed on approaching the zero-charge point, which increases from K^+ to Li^+. In the case of NaF, and particularly LiCl, the minimum remained on the corrected curves.

In contrast to the discharge of $S_2O_8^{2-}$ examined, the corrected Tafel relations for the reduction of $Fe(CN)_6^{3-}$ on mercury are concave toward the potential axis. The slopes of the linear sections of the curves in the region of high values of $-\varphi$ lead to the values $\alpha_0 = 0.16$ in a base electrolyte of LiCl (in accordance with the value obtained previously in [8]), 0.17 in a base electrolyte of KCl, and 0.19 in a base electrolyte of CsCl. In the initial section, the corrected Tafel relations for a base electrolyte of CsCl also have a steeper slope than in other cases.

If it is assumed, as is done in the derivation of Eq. (1), allowance for ψ_0 makes it possible in principle to give an accurate relation of the effective anion concentration to the potential and volume concentration, and that for the reduction of anions with a constant effective concentration of anions, the Tafel equation holds, then it is possible to consider the reasons for the observed deviations of the corrected Tafel relations from linearity. A possible reason for the appearance of a minimum on the corrected Tafel relations is slight specific adsorption of $S_2O_8^{2-}$, which leads to higher process rates close to the zero-charge point than might be expected on the basis of purely electrostatic considerations. Another factor which is not considered in the derivation of Eq. (1) is the discrete structure of the double layer. It is probable that this may be allowed for in a first rough approximation by considering separately the interaction of the anion with the nearest cation, leading to the formation of some form of ion pair in the double layer, and still calculating ψ_0 from the classical theory to allow for the effect of other cations. As follows from the positions of the corrected Tafel relations, the interaction with the nearest cation falls in the sequence $Cs^+ > K^+ > Na^+ < Li^+$. The fact that the corrected Tafel relation is close to linear in the case of CsCl may be explained by the mutual compensation of two effects, namely, a decrease in the amount of specifically adsorbed $S_2O_8^{2-}$ with an increase in $-\varepsilon$ and a simultaneous increase in the Cs^+ concentration. The role of the latter factor falls in the series $Cs^+ > K^+ > Na^+ > Li^+$. This factor determines the form of the corrected Tafel relation for the reduction of $Fe(CN)_6^{3-}$, which is not adsorbed specifically and bears a high negative charge.

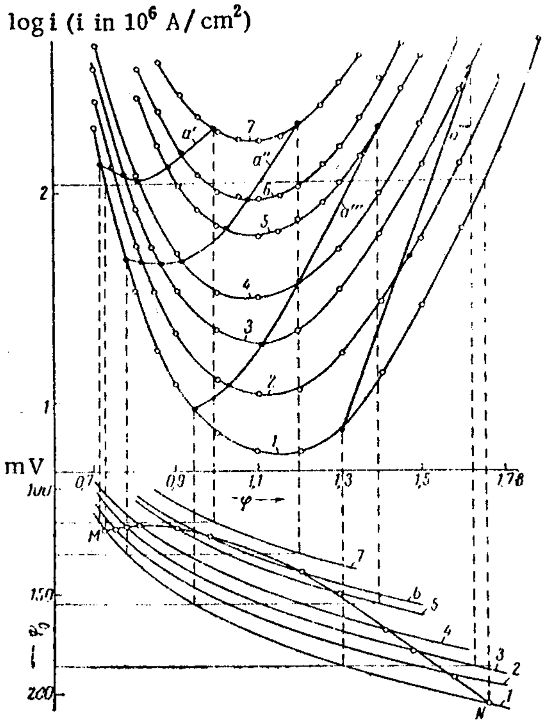

Fig. 2. Graphical analysis of curves for the reduction of 10^{-3} N $Na_2S_2O_8$ in the presence of NaF at the following concentrations: 1) $3 \cdot 10^{-3}$ N; 2) $5 \cdot 10^{-3}$ N; 3) $7 \cdot 10^{-3}$ N; 4) 10^{-2} N; 5) $1.5 \cdot 10^{-2}$ N; 6) $2 \cdot 10^{-2}$ N; 7) $3 \cdot 10^{-2}$ N.

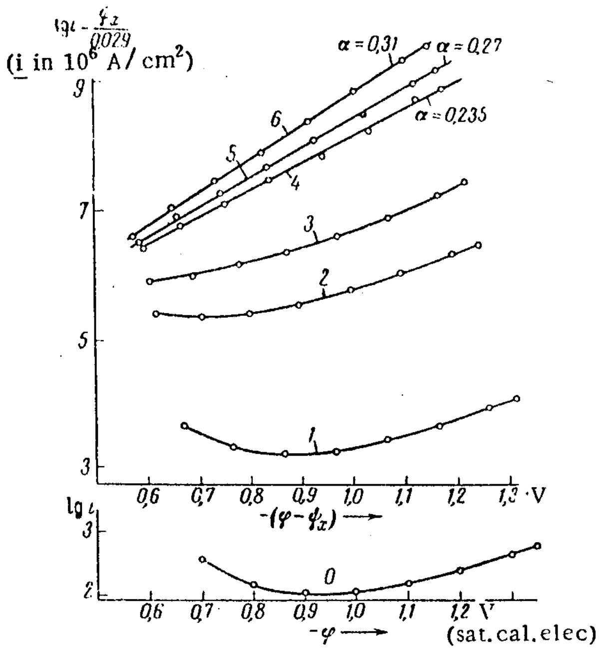

Fig. 3. Relation of the rate of reduction of 10^{-3} N $Cs_2S_2O_8$ in the presence of $2 \cdot 10^{-3}$ N CsCl to the potential (0) and corrected Tafel curves, calculated on the assumption that the center of the particle in the transition state lies at distances of 55.4 A (1), 11.08 A (2), 5.54 A (3),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

The value of α_0 for the reduction of $S_2O_8^{2-}$ was also determined by other methods, which led to results that agree with the conclusions from Fig. 1. Figure 2 shows the determination of α_0 by Gierst's graphical method [9]. The curves a connect points corresponding to the condition ψ_0 = const. As follows from Eq. (1), the slope of these curves $\left(\frac{\partial \lg i}{\partial \varphi}\right)_{\psi_0} = -\frac{\alpha_0 F}{2{,}3RT}$ and is independent of n_1. In the initial section, curves a' and a" have a slight negative slope and only the line a‴ in the region of high values of φ leads to $\alpha_0 = 0.30$. The curve MN in the lower part of Fig. 2 represents the relation $\psi_0 - \varphi$ for log i = const. At high values of φ, there is a linear section on the curve whose slope $\left(\frac{\partial \psi_0}{\partial \varphi}\right)_{\lg i} = -\frac{\alpha_0}{n_1 + \alpha_0}$ when $n_1 = -2$ also gives $\alpha_0 = 0.30$.

We determined the rate of $S_2O_8^{2-}$ reduction at φ = const to $\psi_0 F/2.3RT$ with a base electrolyte of NaF, which was represented by straight lines with a slope of 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 V, and 2.3 at −1.6 V. When Eq. (1) holds, this slope equals $(\alpha_0 - n_1)$. The results we obtained differ from Gierst's conclusions [9].

Let us now consider the case where the center of the charge of the transition state lies at some constant distance x from L_H in the diffuse parts of the double layer. Figure 3 gives the corrected Tafel relations for the reduction of 10^{-3} N $Cs_2S_2O_8$ in the presence of $2 \cdot 10^{-3}$ N CsCl, calculated for this case with various values of x. The corresponding values of ψ_x were found from Gouy's theory. As the center of the reacting particle moves from L_H into the depth of the solution, there is first a gradual decrease in the slope of the corrected Tafel relation. However, right up to a distance of approximately 0.6 A, the change in slope is small and is still within the limits of experimental error. Subsequently, together with a decrease in the slope, curvature of the corrected Tafel relations appears. Thus, if it is assumed that the constant α reflects some real law, it is necessary to exclude assumptions of distances between the center of the charge and L_H exceeding about 3-4 A in the case of $S_2O_8^{2-}$. The corrected Tafel relations for the reduction of $Fe(CN)_6^{3-}$ may be straightened by assuming that the reaction occurs at a distance of about 10 A from L_H. As this gives the improbably low value $\alpha \simeq 0.05$, the elucidation of the physical meaning of the results obtained requires further investigation.

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], it is possible to obtain the following relation 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 the charge in the transition state and L_H to the thickness of the dense part of the double layer. From Eq. (4) it follows that the corrected Tafel relation should remain linear when $\lambda > 0$ if it is linear when $\lambda = 0$. However, the slope of the corrected Tafel relation should fall in the case of cations and rise in the case of anions. Thus, when $n_1 = 1$, $\alpha_0 = 0.50$ and $\lambda = 0.50$, the value of α is 0.25. When $\lambda = 0.08$, $n_1 = -2$ and $\alpha_0 = 0.30$, the value of α is found to be 0.50, and when $n_1 = -3$ and $\alpha_0 = 0.16$, the value $\alpha = 0.50$ may be obtained with $\lambda = 0.097$. Thus, the determination of α depends to a great extent on the assumptions on the position of the charge center of the transition state in the dense layer.

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