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Abstract

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ON THE DETERMINATION OF THE CHARGE OF A REACTING PARTICLE FROM THE DEPENDENCE OF ELECTROREDUCTION KINETICS ON POTENTIAL AND SUPPORTING-ELECTROLYTE CONCENTRATION

Assuming equilibrium between the transition state of the reaction and the reacting particles in solution (the theory of delayed discharge), allowance for the influence of the double layer (d.l.) leads to the following expression for the rate constant k of a one-electron reduction reaction (1):

$$k = k_0 \exp \frac{F}{RT} \left[-\alpha(\varphi - \psi_1) - n_1 \psi_1 \right], \qquad (1)$$

where n_1 is the charge of the reacting particle in the bulk of the solution, ψ_1 is the potential at the point where the center of charge of the transition state of the reaction is located, determined by the other charged particles, φ is the metal-electrolyte potential difference, $0 < \alpha < 1$. To test equation (1), it is necessary to know the dependence of ψ_1 on φ and on the supporting-electrolyte concentration, which is connected with certain assumptions about the structure of the d.l. The simplest assumption, according to which ψ_1 may be equated to the mean value of the potential in the outer Helmholtz layer (ψ_0 of Grahame), is not justified in all cases. The calculation of ψ_0 itself contains a number of approximations (for example, neglect of the discreteness of the d.l. structure, surface filling, etc.). From the observed deviations from equation (1), conclusions have been drawn about a difference between the charge in the surface layer and the charge in the bulk of the solution (formation of ion pairs), and also about other forms of interaction of the reacting anion with cations of the d.l. ([2]). We shall show that, at least in the case of a surface carrying a sufficiently high negative charge, one can choose experimental conditions that ensure an unambiguous test of the concept of the influence of the d.l. structure on the kinetics of electrode processes. Let us compare the course of the reaction of addition of an electron to a particle M^n in two systems I and II with identical values of $[M^n]$, satisfying the following conditions.

1. The adsorption of supporting-electrolyte anions Γ_A and the adsorption of the reacting particle are small in comparison with the adsorption of the cation Γ_K, i.e. $|\Gamma_A| \ll |\Gamma_K|$. From this condition, in the case of dilute solutions and not too small values of the charge density ε, it follows that at sufficiently small distances from the surface of separation the concentration of anions may be neglected in comparison with the concentration of cations.

2. In passing from system I to system II the relation

$$\varphi - \frac{RT}{n_2 F} \ln c = \text{const},$$

is fulfilled, where n_2 is the charge, and c the concentration, of the supporting-electrolyte cations. It is assumed that the solution contains cations of only one magnitude of charge. From the fundamental equation of electrocapillarity, in the case of dilute solutions, it follows*

$$d\sigma = -\varepsilon d\varphi - RT\Gamma_A d\ln c - RT\Gamma_K d\ln c \tag{2}$$

(σ is the interfacial tension, metal-solution). Taking into account condition 1 and the condition of electroneutrality, which in our case reduces to $\varepsilon = -n_2\Gamma_{KF}$, we obtain

$$\left(\frac{\partial\varepsilon}{\partial\ln c}\right)_\varphi = -\frac{RT}{n_2 F}\left(\frac{\partial\varepsilon}{\partial\varphi}\right)_{\ln c}, \qquad \varepsilon = f\left(\varphi - \frac{RT}{n_2 F}\ln c\right), \tag{3}$$

which, in combination with condition 2, leads to $\varepsilon = \text{const}$. The invariance of ε also corresponds to the invariance of the course of the potential at sufficiently small distances from the surface, at which condition 1 is fulfilled.

Indeed, conventionally taking the potential in the metal in both systems

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* For nonideal solutions, concentrations must be replaced by activities $a_\pm$.

equal to zero and, writing in this case the expressions for the electrochemical potentials of the cations

$$\mu_K = \mu_K^0 - \varphi n_2 F + RT\ln c$$

at an infinitely large distance from the interface, we arrive at the conclusion that μ_K is equal when condition 2 is fulfilled. Since in equilibrium near the interface, in accordance with condition 1, only cations participate, it follows from the equality of μ_K that the composition and structure of the surface layer are the

same on passing from system I to system II.* Hence follows the invariance of the quantity $\varphi - \psi_x$ on passing from system I to II, and consequently the relation

$$\psi_x = \text{const} + \frac{RT}{n_2 F} \ln c, \tag{4}$$

where ψ_x is the potential at a distance x from the interface (here and below the potential is measured from a point in the bulk of the solution). Thus, study of the kinetics of processes in systems for which condition 2 is fulfilled makes it possible to reveal the influence on the rate of the process of the potential difference between the point at which the reacting particle is located in the surface layer and the bulk of the solution, with complete constancy of the remaining conditions of the reaction. If the bulk concentration of the reacting particle is kept constant, its concentration near the electrode surface (at distances at which condition 1 is fulfilled) changes proportionally to $\exp[-n_1\psi_{xF}/RT]$. Consequently, the rate of the process is proportional to c^{-n_1/n_2}, or

$$(\partial \ln i/\partial \ln c)_{\varphi - \frac{RT}{n_2 F}\ln c} = -n_1/n_2. \tag{5}$$

This conclusion does not depend on the assumptions on which the theory of the diffuse double layer is based, and remains valid for any surface coverages, as well as in the presence of specific adsorption of cations and of the reacting particle, provided only that condition 1 is fulfilled.** The result also does not depend on the nature of the interaction of the reacting particle with the cations of the double layer, in particular on the formation of ion pairs in the double layer. Therefore, investigation of the dependence of the kinetics of the process on c cannot serve as a diagnostic criterion for determining the charge of the reacting particle in the double layer. Consideration of the equilibrium between ion pairs in the bulk and at the surface leads to the same result ([4]).

Comparison of the kinetics in systems for which the condition

$$\varphi - \frac{RT}{n_2 F} \ln c = \text{const}$$

is fulfilled was first used for a rigorous derivation of the independence of the hydrogen overvoltage from the concentration in acid solutions not containing an indifferent electrolyte ([5]). Equations of type (5) were also applied by Hirst ([2]) in considering the mechanism of reduction of certain cations and anions; however, he justified them differently, which in part explains the difference in interpretation of the results as compared with ours. In the case of reduction of $S_2O_8^{2-}$ in a NaF background there is also a difference between the experimental data obtained by Hirst and by us. The indicated comparison makes it possible to estimate the upper limit of x. For

Figure 1

Figure 1: Figure 1

The conclusion that the structure and composition of the surface layer are the same requires some qualificatio

∗Instead of considering the equilibrium between the reacting particle in the bulk of the solution and in the su

the probability of the transition state is proportional to

$$\exp\left[-\frac{n_1\psi_{xF}}{RT}-\frac{\alpha(\varphi-\psi_x)F}{RT}\right],$$

which leads to the same result, since $\varphi-\psi_x=\text{const}$.

for this, however, one must already resort to a definite picture of the structure of the diffuse double layer. From comparison of the course of the potential in the diffuse layer in Fig. 1, calculated according to Gouy' s theory, it follows that violation of the invariance of the quantity $\psi_x-\frac{RT}{n_2F}\ln c$ on passing from a 10^{-3} to a $10^{-2}N$ solution occurs at distances exceeding 15 Å from the outer Helmholtz plane, and on passing from a 10^{-2} to a $10^{-1}N$ solution—at distances >5 Å. It should be noted that in the case when equilibrium is not maintained between the transition state of the reaction and the reacting particles in the solution, analysis of the dependence of $\ln i$ on $\ln c$ also leads to the charge of the particle in the bulk of the solution*.

Fig. 1. Distribution of the potential in the diffuse layer, counted with respect to the potential at the boundary of the compact and diffuse parts of the double layer, for solutions of a 1–1 valent electrolyte at concentrations: 1–10^{-1}, 2–10^{-2}, 3–$10^{-3}N$ at $\varepsilon=-10\,\mu\text{C/cm}^2$

Thus, the possibility of a rigorous determination of the value n_1 depends only on how accurately condition 1 is fulfilled. The latter can be checked independently of kinetic measurements, from ε,φ-curves or from the shift of the descending branch of electrocapillary curves as a function of c. As follows from the measurements of A. N. Frumkin ([7]), and also from the calculated ε,φ-curves for solutions of LiCl, NaF, KCl, and CsCl of various concentrations according to the data of ([8]) and ([9]), condition 1 is fulfilled for the solutions studied within the accuracy of the measurements.

The method considered for calculating n_1 can also be applied in the case when the reducing anion R^{n_1} is obtained as a result of a preceding dissociation reaction

$$A^n \rightleftarrows R^{n_1} \pm pX^m \quad (n = n_1 \pm mp).$$

If the rate of the process is determined by the slow discharge of R^{n_1} in the presence of equilibrium between the bulk of the solution and the surface layer, and the supporting electrolyte has no influence on the ratio $[A^n] : [R^{n_1}]$, then analysis of the dependence of $\ln i$ on $\ln c$ will lead to the charge of R^{n_1}. If the added electrolyte contains anions capable of affecting the chemical equilibrium, then the violation of the condition of constancy of the bulk concentration of R^{n_1} must be taken into account. When R^{n_1} and A^n are reduced simultaneously, the course of the curve in the coordinates $\ln i$—$\ln c$ must depend on the ratio $[A^n] : [R^{n_1}]$, φ, and c, as well as on the change in the ratio $[A^n] : [R^{n_1}]$, if the added electrolyte contains X^m. The role of the more highly charged anion in the discharge process must decrease with decreasing c and increasing $-\varphi$, in accordance with the resulting increase of $-\psi_1$. If the rate of the process is determined by the slow establishment of equilibrium in the indicated reaction and the thickness of the reaction layer is small in comparison with the thickness of the diffuse layer, then, taking into account for A^n

Indeed, according to Levich' s theory ([6]), the rate constant for reduction of an anion in a 1—1 valent support

where λ is the Debye length. Using (4) and taking into account the inverse proportionality of λ to $\sqrt{c}$, we ob

$$\left(\frac{\partial \ln i}{\partial \ln c}\right)_{\psi - \frac{RT}{n_2 F}\ln c} = -\frac{n_1}{n_2}.$$

and X^m, which are in equilibrium with the bulk of the solution, the Boltzmann distribution, we arrive at the conclusion that the proposed method again gives the charge R^{n_1}. Thus, while making it possible to draw a conclusion about the magnitude of n_1, consideration of the dependence $\ln i - \ln c$ does not answer the question of whether the rate of the process is determined by a chemical reaction preceding the discharge in the double layer or by a slow discharge.

Checking relation (5) for the reduction of H_3O^+ on mercury according to the data ([10,11]) leads to values of n_1 close to 1. Calculation of n_1 for the reduction of $Fe(CN)_6^{3-}$, according to the data ([4]), gives -2.7 in a LiCl background and -3.0 in a KCl and CsCl background. We measured, at a mercury dropping electrode, polarization curves for the reduction of 10^{-3} N $Na_2S_2O_8$, $K_2S_2O_8$, and $Cs_2S_2O_8$ in backgrounds of various concentrations of, respectively, NaF and NaCl (from $3 \cdot 10^{-3}$ to $3 \cdot 10^{-2}$ N), KCl (from $2 \cdot 10^{-3}$ to 10^{-2} N), and CsCl (from $5 \cdot 10^{-4}$ to $5 \cdot 10^{-3}$ N), and also in a solution of 10^{-3} N $Na_2S_2O_8$ in the presence of various concentrations of LiCl + NaCl (from 10^{-2} to $7 \cdot 10^{-2}$ N),

Fig. 2. Dependence of the reduction rate of 10^{-3} N $Na_2S_2O_8$ on potential in the presence of NaF in concentrations: 1 —$3 \cdot 10^{-3}$, 2 —$5 \cdot 10^{-3}$, 3 —$7 \cdot 10^{-3}$, 4 —10^{-2}, 5 —$1.5 \cdot 10^{-2}$, 6 —$2 \cdot 10^{-2}$, 7 —$3 \cdot 10^{-2}$ N.

Fig. 2. Dependence of the reduction rate of 10^{-3} N $Na_2S_2O_8$ on potential in the presence of NaF in concentrations: 1 $-3 \cdot 10^{-3}$, 2 $-5 \cdot 10^{-3}$, 3 $-7 \cdot 10^{-3}$, 4 -10^{-2}, 5 $-1.5 \cdot 10^{-2}$, 6 $-2 \cdot 10^{-2}$, 7 $-3 \cdot 10^{-2}$ N

Figure 2: Fig. 2. Dependence of the reduction rate of 10^{-3} N $Na_2S_2O_8$ on potential in the presence of NaF in concentrations: 1 $-3 \cdot 10^{-3}$, 2 $-5 \cdot 10^{-3}$, 3 $-7 \cdot 10^{-3}$, 4 -10^{-2}, 5 $-1.5 \cdot 10^{-2}$, 6 $-2 \cdot 10^{-2}$, 7 $-3 \cdot 10^{-2}$ N

with the ratio $[Li^+] : [Na^+]$ maintained equal to 10 : 1. The curves in solutions with additions of NaF and NaCl practically coincided at potentials more negative than the p.z.c. After introducing the correction for concentration polarization according to the theory of Meiman–Bagotsky ([4]), n_1 was calculated, as is shown in Fig. 2 (the lines aa connect points corresponding to the condition $\varphi - \frac{RT}{n_2 F} \ln a_{\pm} = \text{const}$). The calculated averages, for different $-\varepsilon$, of the quantity n_1 are -1.78 in the LiCl + NaCl background, -1.85 in the NaF background, -1.90 in the KCl background, and -1.93 in the CsCl background, and are the closer to $n_1 = -2$, the larger is $-\varepsilon$. The conclusion drawn by Gierst ([2]) about the different charge of the reacting particle in the reduction of $S_2O_8^{2-}$ at potentials of the descending and ascending branches of the curve is not confirmed. The lower values of n_1 obtained in the LiCl background can apparently be explained by the fact that, in this case, owing to the lower rate of the process in this background, higher concentrations of additives were used, as a result of which condition 1 was less well fulfilled.

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