

FRACTIONAL NUMBER OF ELECTRONS TRANSFER PHENOMENON IN THE KINETICS OF ELECTRODE REACTIONS

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A necessary condition for the appearance of effective transfer of a fractional number of electrons during individual elementary steps of an electrochemical reaction is the presence in solution of an excess of foreign electrolyte, whose ions make the main contribution to the electric double layer charge. In the systems, metal-metal ions (e.g., a metal salt melt) the phenomenon of effective transfer of a fractional number of electrons cannot be of great importance.

Another physical condition is the appreciable adsorption of the substances participating in electrochemical transformations which results in marked change in the double layer structure (in the double layer capacity in particular) when these substances are introduced into solution.

At present, there exists no quantum theory of an elementary act of electrochemical reactions which would take account of the effective transfer of a fractional number of electrons. Therefore, it is essential to analyse the electrochemical kinetic equations using the Bronsted relation just as it was done by A. N. Frumkin in the case of transfer of an integral number of electrons.

The simplest electrochemical reaction in which effective transfer of a fractional number of electrons is possible includes two adsorption steps with one adsorption state. For such electrochemical reactions one can obtain concrete values for the numbers of electrons transferred during individual adsorption steps from the thermodynamic data on the electrode alone without resorting to the results of kinetic measurements.

The adsorption of substances, for which the dependence of the work of adsorption on the electrode potential obeys the quadratic law, always involves effective transfer of a fractional number of electrons, which depends linearly on the electrode potential.

In kinetic equations of the Tafel type the presence of effective transfer of a fractional number of electrons formally manifests itself in the fact that the ordinary product of the number of electrons and the potential is substituted by the integral of the effective fractional number of electrons with respect to the potential.

The transfer of a fractional number of electrons can be very effectively studied by the impedance measurements. But the electrochemical system in which constant faradaic current is possible proves to be rather complicated from the methodology point of view. These methodology difficulties will be decidedly overcome and then the description of the mechanism of particular electrochemical reactions will include the data on transfer of a fractional number of electrons.

Keywords : Fractional Number of Electron Transfer; Kinetics; Electrode Reactions; Bronsted Relation; Gibbs Adsorption Equation

THE concept of transfer of a fractional number of electrons at separate adsorption stages of an electrochemical reaction came to be used in theoretical electrochemistry comparatively recently. On the other hand, in essentially adsorption phenomenon the transfer of a fractional number of electrons has usually been taken into consideration (Frumkin, 1979). In this connection it suffices to point to the fact that the conventional form of the Gibbs equation adsorption for an ideally polarizable electrode (equation 1) unambiguously testifies of the presence of transfer of a fractional number of electrons in the adsorption process.

$$-d\sigma = qd\phi + \sum_i \Gamma_i d\mu_i \quad \dots(1)$$

The symbols used in equation (1) are as follows: σ is the surface tension (for simplicity both electrode and electrolyte are assumed to be liquid), q is the charge and ϕ is the potential of the electrode, μ_i and Γ_i are respectively the chemical potential and the Gibbs adsorption of a surfactant numbered i .

In the general case, in accordance with equation (2),

$$q = q(\phi, \Gamma_i) \quad \dots(2)$$

the electrode charge is determined both by the electrode potential and the adsorbed amounts. The partial derivative (3)

$$q_{\Gamma_j} = \partial q / \partial \Gamma_j \quad \dots(3)$$

of the electrode charge with respect to the adsorbed amount of the substance j at constant potential and constant amounts of other surfactants gives us the value of the charge transferred to the electrode through the external circuit during the elementary act of the adsorption process numbered j .

By equation (4) the charge (3) on conversion to the effective number of electrons n_j generally proves to be fractional and besides depends both on the electrode potential and on the adsorbed amounts.

$$-q_{\Gamma_j} = a_j F \quad \dots(4)$$

In equation (4), F is the Faraday constant.

The importance of the concept of an effective number of electrons involved in this or another adsorption process follows from the fact that the adsorption isotherm of a surfactant in the explicit form contains an effective number of electrons. Indeed, in accordance with the Gibbs adsorption equation gives as equation (5),

$$-d(\sigma + \sum \Gamma_i \mu_i) = qd\phi - \sum \mu_i d\Gamma_i \quad \dots(5)$$

where the cross derivatives are equal [equation (6)].

$$-n_j F = \left(\frac{\partial q}{\partial \Gamma_j} \right)_{\phi, \Gamma_i} = - \left(\frac{\partial \mu_j}{\partial \phi} \right)_{\Gamma_i} = - RT \left(\frac{\partial \ln c_j}{\partial \phi} \right)_{\Gamma_i} \quad \dots(6)$$

The right hand side of equation (6) in the form of the derivative of the surfactant bulk concentration is valid only for dilute solutions.

The validity of equation (6) means that the adsorption isotherm a be represented as equation (7)

$$c_s = f_s(\Gamma_s) \exp \left[\frac{F}{RT} \int_{\phi_0}^{\phi} n_s d\phi \right] \quad \dots(7)$$

in which f_s is a function of the adsorbed amounts and does not depend on the electrode potential, R is a gas constant, T is the absolute temperature, ϕ_0 is a certain level from which it is convenient to read the electrode potential.

In the case of the Henry isotherm the function f degenerates into a linear dependence and the effective number of electrons depends only on the electrode potential.

A peculiar situation arises when charge transfer is considered in the absence of a supporting electrolyte excess, e.g., in a certain metal salt solution. In the case of electroreduction of metal cations at a distance from the point of zero charge of the electrode, the electrode charge is unambiguously determined by cation adsorption and thus under such conditions, transfer of a fractional number of electrons is absent. However, in that case transfer of a fractional number of electrons can occur if the metal cation discharge passes through several, and not one, adsorption states.

Let us consider now an electrochemical reaction in the presence of a supporting electrolyte excess.

In the simplest case an electrochemical reaction accompanied by adsorption of reacting particles, two adsorption stages and one adsorption state are involved (Frumkin *et al.*, 1952). During the first adsorption stage n_1 electrons and during the second adsorption stage n_2 electrons are effectively transferred. Taken separately, the effective number of electrons can be fractional and depend on the electrode potential as well as on the surface concentration A , of the reacting particles, in the adsorbed state (Senda & Delahay, 1961; Lorenz & Salie, 1961; Delahay, 1966; and Lorenz, 1971). The sum of the effective numbers of electrons n_1 and n_2 is equal to an integral number of electrons n corresponding to the overall electrode process.

The quantity n_1 is the number of electrons which it is macroscopically necessary to supply to the electrode *via* an external circuit in order that on completion of an elementary act of the first adsorption stage, its potential should remain unchanged. The quantity n_2 has a similar sense.

In accordance with the Gibbs adsorption equation for a reversible electrode (Frumkin, 1970),

$$-d\sigma = \Gamma_{ox} d\mu_{ox} + \Gamma_{red} d\mu_{red} \quad \dots(8)$$

where μ is the chemical potentials of a reacting particle; Γ is the Gibbs adsorption of particles (in oxidized and reduced forms) corresponding to the formation of an electric

double layer without supply of electricity *via* an external circuit, and also is in agreement with the Onsager reciprocal equation (Grafov & Pekar, 1971, 1972) arising in the electrode impedance theory, the effective numbers of electrons are expressed in terms of the thermodynamic derivatives-equation (9) :

$$n_1 F = (\partial \mu_{0\#} / \partial \phi)_A; n_2 F = - (\partial \mu_{Rd} / \partial \phi)_A \quad \dots(9)$$

treats the chemical potentials of the reacting particles as the functions of the electrode potential ϕ and the adsorbed amount A .

The kinetic equations of the adsorption process with allowance for their activation nature are shown as equations (10, 11 and 12).

$$V_1 = K_{1a} C_{0\#} \cdot \exp [-W_{1a}(\phi)/RT] - K_{a1} A \cdot \exp [-W_{a1}(\phi)/RT] \quad \dots(10)$$

$$V_2 = K_{a2} A \cdot \exp [-W_{a2}(\phi)/RT] - K_{2a} C_{Rd} \cdot \exp [-W_{2a}(\phi)/RT] \quad \dots(11)$$

$$I_1 = n_1 F V_1; I_2 = n_2 F V_2 \quad \dots(12)$$

where V refers to fluxes of reacting particles, K the rate constants, W , activation energies of processes and C , concentration of reacting particles in oxidized and reduced forms near the electrode surface.

The cathodic direction of the current is considered to be positive. Here the simplest case is being treated where the interaction between reacting particles, both in the bulk of the solution and on the electrode surface, can be ignored. For this reason, the particle fluxes vary in direct proportion to their bulk and surface concentrations, and the activation energies W are independent of the surface concentration of particles.

Under the assumption that the kinetics of the adsorption stages of an electrochemical reaction obey the linear Bronsted relations (they are given in the differential form as equations (13) and (14)) (Grafov & Frumkin, 1975).

$$dw_{1a} = \alpha_1 dw_1 \quad dw_{a1} = -\beta_1 dw_1 \quad \dots(13)$$

$$dw_{a2} = \alpha_2 dw_2 \quad dw_{2a} = -\beta_2 dw_2 \quad \dots(14)$$

where α & β are the transfer coefficients, W refers to heats of adsorption stages. We obtain as a corollary the kinetic equations (15 and 16), for the slow charge transfer during the adsorption stages

$$I_1 = I_{10} \left[\frac{C_{0\#}}{C_{0\#,0}} \cdot \left\{ \exp \left(-\alpha_1 \frac{F}{RT} \int_{\phi_0}^{\phi} n_1(\phi) d\phi \right) \right\} \right. \\ \left. - \frac{A}{A_0} \left\{ \exp \left(\beta_1 \frac{F}{RT} \int_{\phi_0}^{\phi} n_1(\phi) d\phi \right) \right\} \right] \quad \dots(15)$$

$$I_2 = I_{20} \left[\frac{A}{A_0} \cdot \left\{ \exp \left(-\alpha_2 \frac{F}{RT} \int_{\phi_0}^{\phi} n_2(\phi) d\phi \right) \right\} - \frac{C_{Rd}}{C_{Rd,0}} \cdot \left\{ \exp \left(\beta_2 \frac{F}{RT} \int_{\phi_0}^{\phi} n_2(\phi) d\phi \right) \right\} \right] \quad \dots(16)$$

where I_1 & I_2 are the electric currents corresponding to the first and second adsorption stages, A , ϕ_0 , I_{10} , I_{20} i.e., surface concentration, electrode potential, exchange currents of adsorption stages under conditions of equilibrium between electrode and solution with concentrations of reactants C , 0. The cathodic potential is considered to be negative.

Thus, when the effective numbers of electrons n_1 and n_2 are potential dependent, the conventional product $n\phi$ of an integral number of electrons and the electrode potential in the kinetic slow charge transfer equations is substituted by the integral $\int n_1 d\phi$ or $\int n_2 d\phi$ of effective number of electrons over the potential.

In some cases the electroreduction of organic substance proceeds *via* a preceding equilibrium adsorption stage which corresponds to the Henry isotherm :

$$B_0 \exp [-a(\phi - \phi_m)^2] \cdot C_{0\pi} = A \quad \dots(17)$$

where B and a are constants, ϕ_m the potential of maximum adsorption, containing a quadratic dependence of the work of adsorption on the electrode potential. Basically, isotherm (17) gives the dependence of the chemical potential of a surfactant on the electrode potential and the surface concentration A . Taking into account (17), we find for the effective number of electrons transferred during the first equilibrium stage of the electrochemical reaction being considered that

$$n_1 = \frac{RT}{F} (\partial \ln C_{0\pi} / \partial \phi)_A = 2 \frac{RT}{F} \cdot a \cdot (\phi - \phi_m). \quad \dots(18)$$

Thus n_2 electrons are effectively transferred during the second of the overall electroreduction process being potential, dependent which is shown below :

$$n_2 = n - 2 \frac{RT}{F} a(\phi - \phi_m), \quad \dots(19)$$

where n refers to the number of electrons of overall process.

Eventually, the completely irreversible second stage of the electroreduction process is described by the kinetic equation (20)

$$I_2 = I_{2m} \frac{C_{0\pi}}{C_{0\pi,0}} \cdot \exp \left(-\alpha_2 \frac{F}{RT} n(\phi - \phi_m) \right) \cdot \exp \left(-\beta_2 a(\phi - \phi_m)^2 \right), \quad \dots(20)$$

where I_{2m} is the exchange current of second stage at potential of maximum adsorption and initial surfactant concentration $C_{0\pi,0}$ β_2 is the anodic transfer coefficient of a second stage.

The experimental measurements give for the quantity $2/RTa/F$, the value in the vicinity of 0.5 reciprocal volts. This means that at the potential widths which are by a half volt distant from the potential of maximum adsorption, the effective number of electrons n_1 transferred during the reversible adsorption stage will be an equal module to a quarter of an electron. At the potential of maximum adsorption no fractional charge transfer takes place.

A fractional charge transfer could most effectively be detected by measuring the impedance of an equilibrium electrochemical system. But an electrochemical system in which a direct faradaic current can flow is a very complicated system from a metrological point of view owing to a large number of independent unknown parameters.

Undoubtedly, these metrological difficulties will be overcome and then, as it seems to us that the description of the mechanism of particular electrochemical reactions will contain the data on the effective fractional charge transfer during individual adsorption stages of complex electrochemical reactions. A good example is the work by Muller (1979) in which experimental data on electrochemical reactions with the transfer of one electron in the overall reaction were explained on the basis of a reaction with effective (partial) adsorption charge transfer steps.

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