LETTERS TO THE EDITOR

DYNAMIC EFFECT OF THE IONIC ATMOSPHERE IN ELECTROCHEMICAL KINETICS WITH EXCESS INDIFFERENT ELECTROLYTE

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In [1], the probability of the elementary act of an electrochemical reaction had been averaged over the configurations of the ions in the double layer on the assumption that their statistical distribution is an equilibrium or quasi-equilibrium distribution. We shall show below how these results can be generalized to the case where there is departure from equilibrium with respect to the reacting ions in the presence of an excess concentration of indifferent electrolyte. The distribution of the indifferent-electrolyte ions is assumed to be an equilibrium distribution, so that the distribution function can be written as

$$\Phi(R, r_1, r_2, \ldots, r_N) = \Phi_z(R)\,\Phi_z(r_1, r_2, \ldots, r_N; R), \tag{1}$$

where $\Phi_Z(R)$ is the distribution function (generally speaking, the nonequilibrium distribution function) for the reacting ions, while $\Phi_Z(r_1, r_2, \ldots, r_N; R)$ is the equilibrium distribution function of the indifferent-electrolyte ions under the condition that the reacting ion A^Z is located at point R:

$$\Phi_z(r_1, r_2, \ldots, r_N; R) = \exp\{[F_z(R) - zv(r_1, r_2, \ldots, r_N; R) - U(r_1, r_2, \ldots, r_N)]/kT\}. \tag{2}$$

Here $zv(r_1, r_2, \ldots, r_N, R)$ is the interaction energy of ion A^Z with all other ions and their images, $U(r_1, r_2, \ldots, r_N)$ is the interaction energy of the indifferent-electrolyte ions with each other and with their images, and $F_Z(R)$ is the free energy.

In the simplest case, where the Brönsted relationship is linear ($E_a = E_a(0) + \alpha\Delta J$), we obtain for the current density, by substituting (1) and (2) into relations (2) and (3) of [1] and integrating over the coordinates,

$$\vec{i} = en\delta RA(R^*) \exp\{-[E_a^0 + \alpha e\varphi + \alpha[U_{z-1}(R^*) - U_z(R^*)] + F_{z-\alpha}(R^*) - F_z(R^*)]/kT\} \cdot \Phi_z(R), \tag{3}$$

where R* is the effective distance at which the reaction takes place, δR is the reaction-layer thickness, E_a^0 is the part of the activation energy that is independent of potential, $A(R^*)$ is the preexponential factor in the transition probability, $U_Z(R^*)$ and $U_{Z-1}(R^*)$ are the interaction energies of reactant and product with their own, unscreened images, $F_{Z-\alpha}(R^*)$ is the free energy of the indifferent-electrolyte ions which differs from $F_Z(R^*)$ only by the fact that in point R* one has ion A with charge $z-\alpha$ rather than with charge z, and α is the Brönsted symmetry factor (the transfer coefficient). The free energies $F_Z(R^*)$ and $F_{Z-\alpha}(R^*)$ depend on potential, in contrast to quantities F_Z and $F_{Z-\alpha}$ in [1]. The result is readily generalized to the case of a nonlinear Brönsted relationship. The method is applicable, both to stationary and to nonstationary processes. The only necessary condition is the preservation of a Boltzmann distribution for the indifferent-electrolyte ions.

LITERATURE CITED

1. R. R. Dogonadze and A. M. Kuznetsov, Élektrokhimiya, 11, 3 (1975).

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