INFLUENCE OF THE DOUBLE LAYER ON HYDROGEN ION DISCHARGE

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UDC 541.13

The influence of the double layer on electrochemical reaction kinetics can in many cases be described by the model of a self-consistent equilibrium distribution of potential [1-3]. But a theoretical analysis of the laws of charge transfer across polarized interfaces shows [4-6] that electrochemical reaction rate is determined by the fine structure of the electric double layer; this structure arises from the "electrostatic image" forces and from interaction forces between the discrete charges of the reactants and the dielectrically inhomogeneous medium formed by the solvent molecules in the layer next to the electrode. These forces are displayed in a number of electrochemical experiments as "discreteness-of-charge effect." This effect can be observed most clearly when measuring the equilibrium adsorption potential drop as a function of the bulk concentration of a surface-active electrolyte (the Esin–Markov effect). An analysis of kinetic data for the electrochemical discharge of hydrogen ions at mercury [7, 8] also leads to the result that the discrete nature of the reacting species and the fine structure of the double layer must be taken into account. The process just mentioned follows the scheme

$$H_3O^+ + e \rightarrow H_{ads} + H_2O,$$

and can be described by the following kinetic equation:

$$\eta = \frac{1-\alpha}{\alpha}\varphi(x_0) + \frac{kT}{e\alpha}\ln(i/K^* c_0^{1-\alpha}), \quad (1)$$

when the generally adopted approach to the analysis of double-layer effects introduced by Frumkin [1, 3] is used. Here η is the hydrogen overpotential; α is the macroscopic electron transfer coefficient; $\varphi(x_0)$ is the mean potential (as defined by the Gouy–Chapman theory) in the plane $x = x_0$, where the discharge act takes place; i is the current density; K* is a dimensional factor which does not depend on electrode potential; and c_0 is the bulk concentration of H_3O^+ ions.

An appreciable decrease of hydrogen overpotential was observed experimentally in [7, 8] in the presence of specifically adsorbing anions. Thus, in the mixed solutions 1 N HCl + 2 N KCl and 1 N HCl + 2 N KI, the hydrogen overpotential at a current density of $i = 10^{-4}$ A/cm^2 decreased by about 190 mV when the Cl^- ions were replaced by I^- ions. On the assumption that this decrease was due exclusively to a change in the negative direction of the potential, $\varphi(x_0)$, in the plane of discharge (owing to specific adsorption of iodide ions), and that the plane of discharge coincided with the outer Helmholtz plane ($\varphi(x_0 = \psi_0)$, then this change would imply a very significant increase in hydrogen ion concentration (approximately by a factor of 2000) at the outer Helmholtz plane, but this is not observed experimentally.

In order to remove the contradiction mentioned above, Frumkin [3] suggested that hydrogen ion discharge is accomplished via an intermediate state (activated complex), and that the center of charge of the activated complex is located in a plane which is much closer to the electrode than the plane where the centers of the hydrogen ions are located. Quantity $\varphi(x_0)$ appearing in Eq. (1) represents the potential in the plane where the activated complex is located, according to its physical significance; therefore, in the presence of surface-active ions (e.g., I^-), it can assume large negative values and thus produce a marked acceleration of discharge. The potential outside the Helmholtz layer (where the hydrogen ions are found) remains relatively low under these conditions, so that the adsorption of these ions does not change markedly.

A qualitative explanation of the special features of discharge which is not associated with the idea of different potentials in the planes of location of the centers of the ions

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 0038-5387/79/1505-0636$07.50

undergoing discharge and of the activated complexes has been offered in [9]. This explanation was based on the assumption that the discharge act occurs in a plane corresponding to direct contact of the hydrogen ions with the electrode. In other words, it was suggested that only ions which have penetrated into the Helmholtz layer are discharged at the electrode. The local concentration of these ions is much lower than that at the outer Helmholtz plane and in the diffuse part of the double layer; this is due to interaction with a force field which has the tendency to expel the ions from the Helmholtz layer. In [9], the nature of this field was seen in connection with the properties of the structured solvent layer at the electrode, and the drastic decrease in the concentration of reactant ions upon their penetration into the compact layer was described by introducing an empirical factor l (much smaller than unity) into the relation for the local concentration of H_3O^+ ions:

$$C_s = C_0 l \exp\left\{-\frac{e\varphi(x_0)}{kT}\right\}. \quad (2)$$

Since $l \ll 1$, but $|\varphi(x_0)| > \psi_0$, one can qualitatively explain the observed change in overpotential during anion adsorption. In fact, during the adsorption of anions, the potential $\varphi(x_0)$ becomes much more negative, and according to Eq. (1) causes a decrease in η. But this is not attended by any conspicuous adsorption of hydrogen ions, since the bulk of the cations constituting the double layer is located outside the Helmholtz layer, where the potential changes very little during anion adsorption.

In [6], a general expression for the equilibrium concentration of ions in arbitrary dielectric media, in particular inside the Helmholtz layer, was suggested:

$$C_s = C_0 \exp\left\{-\frac{w(x_0)-w(\infty)}{kT}\right\}. \quad (3)$$

Here $w(x)$ is the system's free energy change when a given ion is added to point x_0 while the other solution components have their equilibrium distribution; $w(\infty)$ is the value of this quantity in the bulk of the solution. Quantity $w(x)$ includes, both the specific interactions of the ion with metal and solvent near the electrode ($w_{sp}(x)$) and the electrostatic forces, including coulombic interaction of the ion with the solvent, the metal electrons, and the "ionic atmosphere," as well as interactions between the ions themselves ($w_{el}(x)$):

$$w(x) = w_{sp}(x) + w_{el}(x). \quad (4)$$

It is convenient to separate the interaction energy between the ion and the solvent from $w_{el}(x)$:

$$w_{el}(x) = \frac{e^2}{2R}\left(\frac{1}{\varepsilon(x)} - \frac{1}{\varepsilon(\infty)}\right) + \bar{w}_{el}(x), \quad (5)$$

where $\varepsilon(x)$ is the dielectric permittivity in the point where the ion is located, and R is its radius. In relation (5), the interaction energy with the solvent (the term in round brackets) was written down in the Born approximation. This approximation does not include the influence of the metal phase on the local field created by the ion in the inhomogeneous dielectric medium.

For small ions, quantity $\bar{w}_{el}(x)$ can be calculated by the Güntelberg charging method:

$$\bar{w}_{el}(x) = e\int_0^1 \lim_{r' \to r}\left\{\Phi(r', r, e\tau) - \frac{e\tau}{\varepsilon(r)|r'-r|}\right\} d\tau, \quad (6)$$

where Φ is the potential created in point r' by an ion with charge $e\tau$, located at point r and by the other charges of the system in their equilibrium distribution.

To find quantities Φ and $\bar{w}_{el}(x)$ one must specify the dielectric properties of the medium, i.e., the actual form of function $\varepsilon(x)$ inside the Helmholtz layer. It is not permissible here to use the model of a "dielectric step," where the function $\varepsilon(x)$ undergoes a discontinuous change at the outer Helmholtz plane ($x = d$); the presence of such a step is equivalent to the existence of an infinitely high potential barrier at $x = d$ which would prevent the ions from penetrating into the Helmholtz layer.

For the model with a continuous variation of $\varepsilon(x)$, quantities Φ and $\overline{w}_{el}(x)$ were calculated in [5]. Because of the small size of the characteristic distance (comparable to quantity d) over which a marked change in dielectric permittivity is occurring inside the Helmholtz layer, function $\varepsilon(x)$ was approximated by a sectionally linear distribution:

$$\varepsilon(x)=\begin{cases}\varepsilon_1=\text{const} & 0\leqslant x\leqslant x^*,\\ ax+b & x^*\leqslant x\leqslant d,\\ \varepsilon_0=\text{const} & d\leqslant x<\infty,\end{cases} \tag{7}$$

where $a = (\varepsilon_0 - \varepsilon_1)/(d - x^*)$ and $b = (\varepsilon_1 d - \varepsilon_0 x^*)/(d - x^*)$.

The calculations performed in [5] showed that for ions of a sufficiently small size, the discreteness-of-charge effect is determined chiefly by the first term in expression (5), while function $\overline{w}_{el}$ can be approximated by a potential-energy distribution calculated via the Poisson–Boltzmann equation. As a result one obtains relation (2) for the concentration c_s, with the quantity γ given by

$$\gamma=\exp\left\{-\frac{1}{kT}\left[\frac{e^2}{2R}\left(\frac{1}{\varepsilon_1}-\frac{1}{\varepsilon_0}\right)+w_{sp}(x_0)-w_{sp}(\infty)\right]\right\}. \tag{8}$$

Quantity γ, which characterizes the resistance of the Helmholtz layer against penetration of reactant ions to the electrode, is very sensitive to the values used for the parameters of dielectric inhomogeneity of the double layer (parameters $\varepsilon_1/\varepsilon_0$, and x^*/d when the model distribution (7) is used). Thus, quantity γ increases by approximately an order of magnitude (from 10^{-8} to 10^{-7}) when parameter $\varepsilon_1/\varepsilon_0$ changes from 0.08 to 0.12 (for $x^*/d = 0.5$). An increase in parameter x^*/d (for $\varepsilon_1/\varepsilon_0 = 0.1$) from 0 to 1 causes γ to decrease from 10^{-4} to 10^{-8}. The observation that coefficient γ remains much smaller than unity for all values of the characteristic double-layer parameters provides an argument for the assumption that the ions undergoing discharge are penetrating into the Helmholtz layer; when making this assumption one obtains a full explanation for the drastic decrease in hydrogen overpotential which occurs during specific adsorption of anions.

LITERATURE CITED

1. A. N. Frumkin, Z. Phys. Chem., 164, 121 (1933).
2. R. Parsons, Adv. Electrochem. Electrochem. Eng., 1, 1 (1961).
3. A. N. Frumkin, Adv. Electrochem. Electrochem. Eng., 1, 65 (1961).
4. R. R. Dogonadze and A. M. Kuznetsov, Elektrokhimiya, 11, 3 (1975); 13, 1268 (1977).
5. V. S. Krylov, Élektrokhimiya, 14, 1274 (1978).
6. M. A. Vorotyntsev, Élektrokhimiya, 14, 911, 913 (1978).
7. S. Iofa, B. Kabanov, E. Kuchinskii (Kuchinsky) and F. Chistyakov (Chistjakov), Acta Physicochim. URSS, 10, 317 (1939).
8. Tsa Chuang-Hsin and Z. A. Iofa, Dokl. Akad. Nauk SSSR, 126, 1308 (1959).
9. L. I. Krishtalik, Élektrokhimiya, 6, 1165 (1970); J. Electroanal. Chem., 35, 157 (1972).