ROLE OF Ψ_1-EFFECTS IN THE KINETICS OF ELECTRODE PROCESSES

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The problem of the effect of the structure of the double layer on the rate of electrode reactions is one of the main problems in electrochemical kinetics. The existence of the so-called Ψ_1-effects was first shown by Frumkin who developed a theory for this phenomenon [1]. However, a detailed interpretation of several cases, especially the significant decrease in the hydrogen overvoltage in the presence of adsorbed anions, has, up to now, encountered serious difficulties [2, 3]. The most important difficulty is the fact that a large shift of the Ψ_1-potential, which must be assumed to explain the large decrease in the hydrogen overvoltage in solutions of, for example, iodides, should have led to a significant build-up of hydrogen ions on the electrode surface, and, consequently, to their appreciable adsorption. However, this has not been observed experimentally.

This contradiction was recently again examined by Parsons [4] who assumed that the effect of iodide and other anions is not associated with a Ψ_1-effect but is virtually completely due to an abrupt decrease in the activity coefficient of the activated complex. This leads to a significant acceleration in the reaction, but, since the concentration of the activated complex is small, it does not affect the results of the adsorption measurements. Moreover, the original interpretation of Frumkin, i.e., the presence of Ψ_1-effects, which depend on the solution composition in accordance with the conclusions of the theory of the diffuse double layer, is maintained for phenomena observed in the absence of adsorbed anions. Thus, the conclusion proposed by Parsons is by nature compromising.

As far as the assumption regarding the sharp decrease in the activity coefficient of the activated complex is concerned, completely probable all by itself, it is still inadequate to eliminate the contradiction under consideration. The same factors which affect the activity coefficient of the transition state should in principle affect the activity coefficient for adsorbed hydrogen ions. The decrease in the latter should lead to an increase in the surface concentration of ions, i.e., to the appearance of their significant adsorption.

We recently showed [5] that for a reaction subject to the Brönsted relationship the activity coefficient of the transition state $\gamma^{\neq}$ is associated with corresponding values for the starting substances γ_i and reaction products γ_f by the expression

$$\gamma^{\neq} = \Pi\gamma_i^{\beta}\Pi\gamma_f^{\alpha}, \tag{1}$$

where α is the transfer coefficient, and $\beta = 1-\alpha$.

It is well known that the current depends on the overvoltage η, the ψ_1-potential, and the activity of the hydrogen ions in the double layer $\gamma_s c_s$ (c_s is the surface concentration, γ_s is the corresponding activity coefficient, and c and γ are the same in the volume) in the following way:

$$i = k\frac{c^{-\alpha}\gamma^{-\alpha}c_s\gamma_s}{\nu_{\neq}}e^{\alpha\psi_1 F/RT}e^{\alpha\eta F/RT}. \tag{2}$$

If one substitutes

$$\gamma_s c_s = \gamma c e^{-\psi_1 F/RT} \tag{3}$$

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into this equation and takes expression (1) into account, we obtain

$$i = k' \frac{c^{\beta}\gamma^{\beta}}{\gamma_s^{\beta}} e^{-\beta\psi_1 F/RT} e^{\alpha\eta F/RT}. \quad (4)$$

If we do not observe a significant positive adsorption of hydrogen ions, i.e., $c_s/c \leqslant 1$, it then follows from (3) that

$$\frac{\gamma}{\gamma_s} e^{-\psi_1 F/RT} \lesssim 1,$$

i.e., the product of the corresponding terms which enters into (4) in degree β does not exceed unity, and, consequently, neither the ψ_1-effect nor changes in the activity coefficient can explain the abrupt increase in the reaction rate in the absence of significant adsorption of hydrogen ions.

Parsons was apparently aware of these considerations since he cited [5] but assumed that the results obtained therein were not applicable to iodide solutions since the Brönsted relationship is not observed under the given conditions. The latter assertion is not, however, substantiated. It was based on nonobservance over a definite range of potentials of the Tafel equation, but the reason for this phenomenon may lie not in the invalidity of the Brönsted relationship but, as usually assumed, in the sharp rearrangement of the double layer in the null charge point region. In addition, at lower overvoltages, where the iodide effect reaches a maximum value, the polarization curve again follows the Tafel equation, and one can therefore scarcely doubt the applicability of the Brönsted relationship here.

Another approach, also based on the concept of a low concentration of activated complex, was previously given by Frumkin [3]. He assumed that the charge center of the activated complex lies in a plane considerably closer to the electrode than the plane of distribution of the hydronium ion centers. However, the potential in the plane of the transition complex and not that of the ions enters into the kinetic equation as the ψ_1-potential. ψ_1 can therefore take on large negative values (in the absence of, for example, iodide) causing a strong acceleration of discharge. But, at the same time, the potential in the plane of distribution of ions remains comparatively small so that the adsorption of hydrogen ions is not observed.

This interpretation does not contain contradictions in principle. However, the very assumption of the substantial difference in the position of the ion charge centers and the activated complex requires a special basis. According to the quantum-mechanical theory of proton transfer recently developed by Dogonadze, Kuznetsov, and Levich [6, 7], the activation process is caused by reorganization of the solvent during a fixed quantum state of the proton. Thus, within the framework of the given model the charge centers in the activated and starting states coincide and the explanation considered above is inapplicable. *

In connection with what we have so far presented we deemed it expedient to again examine the problem of the effect of the ψ_1-potential on the rate of an electrode reaction. The treatment presented below is, in a certain sense, a development of ideas expressed by Frumkin, but it does not include the assumption of a different potential in the planes of distribution of the discharging ions and activated complexes. It is based on modern data on the structure of the double layer, from which it develops that the so-called dielectric layer—layer of molecular dimensions (probably a single layer of water)—in which the concentration of unadsorbed ions is markedly decreased, is adjacent to the electrode [9]. It is generally assumed in simplified models that the dielectric layer is free of specifically unadsorbed ions. It is clear, however, that this assumption cannot be strictly true since it is difficult to imagine that the ions would not be free, even if in some degree, to penetrate into the solvent layer closest to the electrode. The very fact of ionic discharge indicates their direct contact with the electrode since otherwise the discharge would be extremely unfavorable, energetically speaking [10].† Thus, we arrive at the conclusion that, in addition to the fundam-

*The recently [8] proposed calculation of the change in the coordinates of a solid particle (in this case, the O atom) for hydrogen evolution does not introduce substantial corrections into this conclusion.

† The hypothesis of the transfer of a proton along the chain of hydrogen bonds through the layer of water molecules adjacent to the electrode does not change anything in principle since it is inapplicable to the discharge of other cations. However, the proximity of the properties of the hydronium ion and the cations of alkali metals, especially potassium, makes it unlikely that fundamental differences exist between them from the point of view of the possibility of their introduction into the surface monolayer of the solvent.

ental portion of ions of the double layer situated in the external Helmholtz plane and in the diffusion cloud, there is a certain number of ions directly touching the electrode. It is precisely these ions which discharge on the electrode. Their concentration is determined not only by the distribution in the field of coulombic forces (Eq. (3)) but also by the additional work associated with the transfer of an ion from the volume of the solution into the structured surface layer of solvent. This is reflected in the introduction into the corresponding expression of the factor $l \ll 1$

$$\gamma_s c_s = l\gamma c e^{-\psi_1 F/RT}. \tag{3a}$$

If there are no specifically adsorbed ions, the ψ_1-potential probably does not markedly differ from the potential of the external plane ψ_0. Thus, if one, to a first approximation, considers the double layer as two successively joined capacitors, one of which corresponds to the dielectrically saturated monolayer of solvent and the other to the following layer bounded on the solvent side by the external Helmholtz plane, then, since the capacitance of the first capacitor C_1 is considerably less than the second C_2 (lower dielectric permeability), the potential drop will chiefly occur in the first layer, and $\psi_1 - \psi_0$ will constitute a small fraction of the dense layer: $\psi_1 - \psi_0 = [C_1/(C_1 + C_2)]\ (\varphi - \psi_0)$.* In the case under consideration, therefore, the dependence of ψ_1 on, for example, the composition of the solutions is close to that for ψ_0, and all the conclusions of the original Frumkin theory remain in force.

If, however, adsorbed ions are absent, ψ_1 is strongly shifted to the negative side (but, in the process, it need not equal the ψ_i-potential of the internal Helmholtz plane), the concentration of discharging ions increases markedly and, consequently, discharge is accelerated. However, no significant changes in adsorption occur in the process because the fundamental mass of the cations formed by the double layer is located in the external Helmholtz plane, the potential of which ψ_0 undergoes only relatively small changes during adsorption of anions.

Thus, the separation of the double layer cations into those found in its external shell and into those in direct contact with the electrode (a considerably smaller portion), which flows out of investigations of the structure of the double layer, permits one to explain the fundamental facts associated with the ψ_1-effects both in the absence and presence of specifically adsorbed ions.

Recently in our laboratories Tsionskii obtained results which are a serious argument in favor of the concept that the overvoltage shift in the presence of iodide is chiefly due to the ψ_1-effect and not to the change in the activity coefficients and similar factors. It turned out that the effect of both iodide and tetrabutylammonium on the distribution coefficient of hydrogen isotopes corresponds exactly to the change in the field acting on the ion, i.e., to the change in the ψ_1-potential calculated from the value of the overvoltage shift [11]. If the decrease in overvoltage were caused by the change in the activity coefficient, its effect would hardly coincide quantitatively with the field effect observed even in the absence of adsorbed additives.

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*If one considers that the penetration of cations into the plane corresponding to ψ_1 shifts ψ_1 to the positive side, the difference between ψ_1 and ψ_0 is less and less dependent on φ; in the limiting case of large build-up of cations in the corresponding plane, ψ_1 depends linearly on $(\varphi - \psi_0)$.