OPTIMUM DISTANCE FOR TUNNELING OF ELECTRONS AND REORGANIZATION OF A SOLVENT

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Attempts to detect the reduction of particles at distances from the electrode exceeding the dimensions of one or two molecules have not yielded positive results, the ions or molecules located in the dense part of the double layer being reduced in all the fairly extensively studied cases. Considering the theoretical possibility of the tunneling of electrons at considerably larger distances, it would be wise to discuss one of the possible causes of this effect.

Electron transfer can occur only after the energy levels of the initial and final states have been equalized. This equalizing of the levels occurs as a result of the reorganization of the medium, which causes a change in the interaction between the charge and the dipoles of the solvent. In the case of an ion located in the dense part of the double layer, only the solvent located in one half space undergoes reorganization in practice. As the ion is removed from the metal to the bulk of the solvent undergoing reorganization, the layer lying between the ion and the metal is added. This results in an increase in the reorganization energy and consequently in an increase in the activation energy of the process. Therefore, although tunneling is entirely possible at large distances, nevertheless, a large activation energy is required to create a situation favorable for such a process, and it does not make a substantial contribution to the total current. Of course, this does not mean that direct contact between the ion and the electrode is necessarily the optimum situation. The monolayer of solvent at the electrode surface may be sufficiently oriented and, thus, not undergo significant orientation. In this, introduction of a discharging ion to the first monolayer will not produce a large gain in the reorganization energy, while the very introduction of the ion into an oriented monolayer must be accompanied by an expenditure of energy. In such a situation it could be more advantageous for the discharging particle to be located in the second monolayer (in the outer, rather than the inner Helmholtz layer). This applies only to reactions without the formation of chemisorbed particles, direct contact with the electrode, of course, being necessary in that case.

However, exclusion of a considerable part of the solvent from the sphere of interaction with the ion in transferring the ion from the bulk of the solvent to the double layer does not lead to a large change in the energy of the system; the gain in the energy of solvation is largely compensated by the energy of interaction with the image of the charge in the metal. However, unlike the interaction with the dipoles, the forces of the image are practically noninertial, i.e., no reorganization energy is needed to change them. Therefore, the equilibrium internal energy changes for electrode processes involving an ion in the double layer and at a certain distance from the metal are similar to each other, while the nonequilibrium values (the activation energy) may differ substantially.

A situation which is analogous in a certain sense to electrode processes occurs in homogeneous redox reactions. In this case, the energy of reorganization also increases as the distance of charge transfer increases, making the distant transfer of electrons not advantageous.

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