# CALCULATING THE PROBABILITY OF ELECTRON TRANSFER IN A POLAR MEDIUM

A. M. Kuznetsov

UDC 541.13

Dogonadze and co-workers [1, 2] used a Hamiltonian model of a polar solvent to calculate by a quantum mechanical method the probability of the elementary act of electron transfer, not accompanied by a deformation of the ion coordination sphere; a random dispersion of vibration frequencies of the longitudinal fraction of the specific polarization of the medium $\vec{P}(\vec{r}, t)$ was assumed. If the inertia polarization fluctuations of the medium $\vec{P}^{in}(\vec{r}, t)$ are entirely classical ($\omega < kT/\hbar$), the calculation can be carried out without the use of a solvent model, basing it only on its macroscopic properties. A semiclassical method can be applied for this purpose [3], using the Fourier components $P_k^{in}(t)$ of inertia polarization $\vec{P}^{in}(\vec{r}, t)$ directly as a coordinate, describing the state of a slow subsystem, and taking them as random functions of time.

The interaction between ions and inertia polarization takes the form

$$-\int \vec{P}^{in}(\vec{r})\,\vec{D}_{i,f}(\vec{r})\,d\vec{r} = -\sum_k P_k^{in}(t)\,D_{ki,f}^{*}, \tag{1}$$

where $\vec{D}_i$ and $\vec{D}_f$ are the inductions of ions i and $f$. The solution of the equations of resolution coefficients of the electron wave function for the electron wave functions of ions i and $f$, in a single passage of the system through an arbitrary point $\{P_k^{in}\}^{\neq}$ of the intersection surface of terms with fixed velocities $\dot{P}_k^{in} \equiv dP_k^{in}/dt$ [3]:

$$W = 1 - \exp(-2\pi\gamma);\quad \gamma = L^2 \Big/ \hbar \left| \sum_k \dot{P}_k^{in}(D_{ki}^{*} - D_{kf}^{*}) \right|, \tag{2}$$

where L is the electron exchange integral.

The intersection surface of the first and last terms is given by the equation

$$E_i - E_f - \left\{\frac{1}{8\pi}\left(1 - \frac{1}{\varepsilon_0}\right)\sum [|D_{ki}|^2 - |D_{kf}|^2]\right\} - \sum_k (P_{k0}^{in})_i(D_{ki}^{*} - D_{kf}^{*}) = \sum_k [P_k^{\neq} - (P_{k0}^{in})_i](D_{ki}^{*} - D_{kf}^{*}) \tag{3}$$

where $E_i$ and $E_f$ are the electron energies of ions i and $f$, $\varepsilon_0$ is the optical dielectric permeability of the medium, and $(P_{k_0}^{in})_i$ is the Fourier component of the equilibrium inertia polarization in the initial state; the term in figure parentheses in Eq. (3) describes the interaction of reagents with inertialess (electron) polarization.

To find the full probability of transfer in the unit time <W>, expression (3) must be neutralized for all possible values of $P_k^{in}$ and $\dot{P}_k^{in}$. From the condition of polarization reality it follows that $P_{-k}^{in} = (P_k^{in})^*$ and $P_{-k}^{in} = (P_{-k}^{in} = (\dot{P}_k^{in})^*$. Therefore, the real and imaginary parts of $P_k^{in}$ and $\dot{P}_k^{in}$ ($k > 0$) can be taken as independent variables. Let us assume that $\mathrm{Re}\,P_k^{in}$, $\mathrm{Im}\,P_k^{in}$, $\mathrm{Re}\,\dot{P}_k^{in}$, and $\mathrm{Im}\,\dot{P}_k^{in}$ represent independent random values, distributed according to the common rule around equilibrium values that correspond to the initial state, for example,

---

Institute of Electrochemistry, Academy of Sciences of the USSR, Moscow. Translated from Élektrokhimiya, Vol. 7, No. 7, pp. 1067-1069, July, 1971. Original article submitted July 14, 1970.

$$f(\mathrm{Re}\,\delta P_k^{in}) = [2\pi\overline{(\mathrm{Re}\,\delta P_k^{in})^2}]^{-1/2}\exp\left[-\frac{(\mathrm{Re}\,\delta P_k^{in})^2}{2\overline{(\mathrm{Re}\,\delta P_k^{in})^2}}\right] \qquad k>0, \tag{4}$$

where $\delta P_k^{in} = P_k^{in} - (P_{k0}^{in})_i$. The mean probability is then expressed by [3]:

$$\langle W\rangle = \frac{kT}{h}\varkappa e^{\frac{S_a}{kT}}\exp\left\{-\left[E_i - E_f - \frac{1}{8\pi}\left(1-\frac{1}{\varepsilon_0}\right)\sum_k(|D_{ki}|^2 - |D_{kf}|^2)\right.\right.$$
$$\left.\left. - \sum_k (P_{k0}^{in})_i(D_{ki}^* - D_{kf}^*)\right]^2 \Big/ 2\sum_k \overline{|\delta P_k^{in}|^2}\,|D_{ki} - D_{kf}|^2\right\}, \tag{5}$$

where

$$S_a = k\ln\frac{\hbar\omega_{\mathrm{eff}}}{kT}. \tag{6}$$

The transmission coefficient $\varkappa$ for adiabatic reactions is equal to unity; in the case of nonadiabatic reactions it takes the form:

$$\varkappa = L^2\left(4\pi^3/\hbar^2\omega_{\mathrm{eff}}^2\frac{1}{2}\sum_k\overline{|\delta P_k^{in}|^2}\,|D_{ki} - D_{kf}|^2\right)^{1/2}. \tag{7}$$

When developing (5) it was assumed that $\overline{(\mathrm{Re}\,\delta P_k^{in})^2} = \overline{(\mathrm{Im}\,\delta P_k^{in})^2} = \frac{1}{2}\overline{|\delta P_k^{in}|^2}$; summation in Eq. (5) is carried out by positive as well as by negative values of k.

The effective frequency in (6) and (7) is determined by the equation

$$\omega_{\mathrm{eff}}^2 = \sum_k \overline{|\delta \dot{P}_k^{in}|^2}\,|D_{ki} - D_{kf}|^2 \Big/ \sum_k \overline{|\delta P_k|^2}\,|D_{ki} - D_{kf}|^2. \tag{8}$$

Thus, all parameters determining the transfer probability are expressed by macroscopic characteristics of the medium: the equilibrium polarization $\overline{(P_{k0}^{in})_i}$ and the least squares of polarization fluctuations $\overline{|\delta P_k^{in}|^2}$, and of polarization derivatives for time $\overline{|\delta \dot{P}_k^{in}|^2}$.

It is taken into account that the equilibrium inertia polarization is related to induction by the equation

$$(P_{k0}^{in})_i = \frac{1}{4\pi}\left(\frac{1}{\varepsilon_0} - \frac{1}{\varepsilon_s(k)}\right)D_{ki}, \tag{9}$$

where $\varepsilon_s(k)$ is the static dielectric permeability of the solvent. Also, in the case of classical fluctuations $\overline{|\delta P_k^{in}|^2}$ is given by [4]:

$$\overline{|\delta P_k^{in}|^2} = \frac{\hbar}{4\pi^2}\int_0^{\omega_{\mathrm{lim}}}\frac{\mathrm{Im}\,\varepsilon(k,\omega)}{|\varepsilon|^2}\,\mathrm{cth}\frac{\hbar\omega}{2kT} \approx \frac{1}{4\pi}\left(\frac{1}{\varepsilon_{\mathrm{lim}}(k)} - \frac{1}{\varepsilon_s(k)}\right)kT \equiv S(k), \tag{10}$$

where $\varepsilon(k,\omega)$ is the complex dielectric permeability of the medium, $\omega_{\mathrm{lim}}\left(<\frac{kT}{\hbar}\right)$ is the upper limit of the adsorption region, S(k) is the Fourier component of the longitudinal part of the spatial correlation function of polarization fluctuation $S(\vec{r}-\vec{r}\,') = \langle\,\delta\vec{P}^{in}(r)\,\delta\vec{P}^{in}(\vec{r}\,')\,\rangle$, and $\varepsilon_{\mathrm{lim}}(k)$ the dielectric permeability at the upper limit of the absorption region (on the strength of the above assumption, that fluctuations of the inertia polarization of the medium are entirely classical, $\varepsilon_{\mathrm{lim}}(k)$ coincides with $\varepsilon_0$). Therefore, the index of the last exponent in (5) can be written as follows

$$-[\Delta J_{if} + E_r]^2/4E_r kT, \tag{11}$$

where $\Delta J_{if}$ is the thermal effect of the process and $E_r$ is given by the equation

$$E_r = \frac{1}{2}\sum_k \frac{S(k)}{kT}|D_{ki} - D_{kf}|^2 = \frac{1}{8\pi}\sum_k \left(\frac{1}{\varepsilon_0} - \frac{1}{\varepsilon_s(k)}\right)|D_{ki} - D_{kf}|^2. \tag{12}$$

From (12) it follows that the energy of transpolarization $E_r$* is the lower, the stronger the spatial correlation of polarization fluctuation, i.e., the smaller S(k).

Equation (8) allows us to assess $\omega_{\mathrm{eff}}$ if the dielectric permeability of the medium $\varepsilon(k, \omega)$ is known. Use can be made here of the fact, that in the case of classical fluctuations the expression for $\overline{|\delta \hat{P}_k^{\mathrm{in}}|^2}$ takes the form

$$\overline{|\delta P_k^{\mathrm{in}}|^2} = \frac{\hbar}{4\pi^2}\int_0^{\omega_{\lim}} \omega^2 \frac{\operatorname{Im}\varepsilon(k,\omega)}{|\varepsilon|^2}\operatorname{cth}\frac{\hbar\omega}{2kT}\,d\omega \approx \frac{1}{2\pi^2}\int_0^{\omega_{\lim}} \frac{\omega^2 \operatorname{Im}\varepsilon(k,\omega)}{\omega|\varepsilon|^2}\,d\omega\cdot kT. \tag{13}$$

If absorption in the medium is characterized by one sharp maximum, $\omega_{\mathrm{eff}}$ practically coincides with the frequency of the absorption band maximum. If the absorption region is diffuse, $\omega_{\mathrm{eff}}$ shifts from the maximum towards higher frequencies.

The method presented here can be applied in the case, when the total inertia polarization can be divided into two parts: the classical ($\omega < kT/\hbar$) and the quantum polarization ($\omega > kT/\hbar$). All deductions made above are formally preserved, however $\varepsilon_0$ in Eq. (12) must be replaced by $\varepsilon_{\lim}$ and L in (7) represents a matrix element, which takes into account not only the change in state of the electron, but also of the high-frequency polarization of the medium. The above semiclassical calculation method is expected to give good results in the case when absorption in the frequency region $\omega \sim kT/\hbar$ can be neglected. If $\operatorname{Im}\varepsilon(k, \omega)/|\varepsilon|^2$ in this region differs essentially from zero, the calculation of the transfer probability for a nonadiabatic reaction must be carried out entirely by the quantum mechanical method [1, 2, 5, 6]. A special examination is required in the case of an adiabatic reaction.

## LITERATURE CITED

1. R. R. Dogonadze, A. M. Kuznetsov, and A. A. Chernenko, Uspekhi Khimii, 34, 1779 (1965).
2. R. R. Dogonadze, A. M. Kuznetsov, and V. G. Levich, Dokl. Akad. Nauk SSSR, 188, 383 (1969).
3. R. R. Dogonadze and A. M. Kuznetsov, Scientific Achievements, Electrochemistry, 1967 [in Russian], VINITI, Moscow (1969).
4. L. D. Landau and E. M. Lifshits, Electrodynamics of Uniform Media [in Russian], Gostekhizdat, Moscow (1957).
5. A. A. Ovchinnikov and M. Ya. Ovchinnikova, Zh. Éksperim. i Teor. Fiz., 56, 1278 (1969).
6. M. A. Vorotyntsev and A. M. Kuznetsov, Deposited at VINITI, No. 1234-69 dep.

---

* The relationship between the reorganization energy $E_r$ and the steric correlation of the fluctuation of the medium polarization, i.e., the steric dispersion of dielectric permeability, was first established in [3]. The relationship between the parameters determining the probability of the transition and the frequency dispersion of the dielectric permeability $\varepsilon(\omega)$ was first shown in [5].