

TRANSFER COEFFICIENT AS A FUNCTION OF REACTION FREE ENERGY IN ADIABATIC PROCESSES

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The transfer coefficient, α , is calculated as a function of reaction free energy while using the system's adiabatic potential-energy surface. It is shown that at moderate values of the reaction free energy, $\alpha(G_0)$ is changing more slowly than in the case of nonadiabatic processes, but the transitions to the barrierless and activationless region occur more rapidly.

The dependence of transfer coefficient α on reaction free energy in homogeneous processes and on potential in electrochemical processes is an important theoretical problem of the elementary act of chemical and electrochemical processes. For the simplest models, current quantum theory of homogeneous and heterogeneous charge transfer reactions predicts a linear dependence of the transfer coefficient on reaction free energy G_0 [1]:

$$\alpha = \frac{1}{2} + G_0/2E_s, \quad (1)$$

where E_s is solvent reorganization energy. The behavior of α in systems where the potential can be varied widely has been studied experimentally in a number of cases [2-8]. It was claimed in some of these papers that the transfer coefficient remained practically unchanged over the potential range investigated [3, 4], while in other papers a change of α with potential was noticed [2, 5-8].

In the present communication we report results obtained when studying the influence of the magnitude of resonance splitting of the system's adiabatic electron terms on the character of function $\alpha(G_0)$.

In the quantum theory of the elementary act of charge transfer processes in polar media, the initial and final state of the system customarily are described with the aid of electron channel terms or potential-energy surfaces of the initial (U_i) and final (U_f) state of the system. The electron terms U_i and U_f are functions of the coordinates, Q_k , of heavy particles (cores) and of the generalized coordinates, q_k , describing solvent polarization. In the general case, the degrees of freedom describing the system can be split into classical ($\hbar\omega_{cl} < kT$) and quantum ($\hbar\omega_{qu} > kT$) degrees; the activation energy in the normal region of the process $|G_0| < E_s$, is determined only by the behavior of the classical degrees of freedom [1].

Let us start the discussion with the simplest case of an electron transfer reaction not attended by rearrangement of intramolecular degrees of freedom. We shall describe the state of the solvent by the single generalized coordinate q . Then U_i and U_f can be written down as

$$U_i = \frac{\hbar\omega}{2} q^2, \quad U_f = \frac{\hbar\omega}{2} (q - q_0)^2 + \Delta I, \quad (2)$$

where ΔI is the equilibrium energy difference of the final and initial state. In the general case, ΔI can be written as $\Delta I = \Delta I_0 + v_f - v_i$, where v_i and v_f are the energies of reactant approach and reaction product separation, while ΔI_0 is the reaction free energy found for infinite separation of the reactants. For the sake of simplicity we shall regard v_i and v_f as zero in the following.

The activation energy of nonadiabatic processes is determined by the intersection point of U_i and U_f , and given by the expression [1]

$$E_a = (E_s + \Delta I)^2 / 4E_s, \quad (3)$$

where $E_s = (\hbar\omega/2)q_0^2$ is the solvent reorganization energy. The expression for $\alpha = dE_a/d\Delta I$ corresponding to (3) coincides with (1) where $\Delta I = G_0$.

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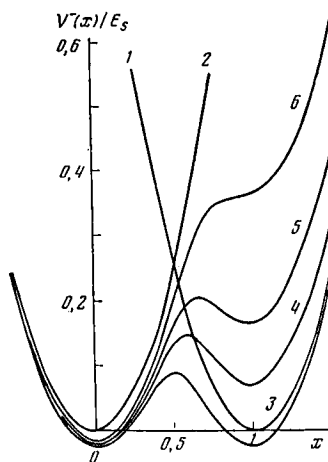


Fig. 1. Nonadiabatic (curves 1 and 2) and adiabatic (curves 3 to 6) electron terms of the system. Curves 3 to 6 correspond to parameters $b = 0.1$ and $y = 0, 0.1, 0.2$, and 0.4 .

A more exact calculation of activation energy should include the distortion of the potential-energy surface caused by the electron exchange integral L . In the general case, the activation energy is determined by the form of the adiabatic potential-energy surfaces $V^\pm$ which, in terms of the two-state approximation, are determined by the relation [9]

$$V^\pm = \frac{U_i + U_f \pm \sqrt{(U_i - U_f)^2 + 4L^2}}{2}. \quad (4)$$

Here the plus sign refers to the upper, the minus sign to the lower adiabatic term (Fig. 1). At low values of L ($|L| \ll E_s$), the adiabatic term V^- to the left of the intersection point of U_i and U_f coincides with U_i , that to the right of the intersection point coincides with U_f . At values of L which are comparable with E_s , the potential-energy surface V^- can markedly differ from U_i and U_f over a wide range of values of coordinate q .

Let us change to the new variable $x = q/q_0$ in expressions (2) and (4). Then V^- can be written as

$$V^- = E_s \frac{2x^2 + (y - 2x + 1) - \sqrt{(y - 2x + 1)^2 + b}}{2}; \quad (5)$$

here $y \equiv \Delta I/E_s$ and $b \equiv 4L^2/E_s$. At relatively small values of y , function $V^-(x)$ has two minima corresponding to the initial and final state of the system, and a maximum between these two minima. From the condition that $dV^-/dx = 0$, on the assumption that L is independent of x , we obtain the equation defining the extreme points $0 \leq x_1 \leq x_2 \leq x_3 \leq 1$:

$$2x - 1 + \frac{y - 2x + 1}{\sqrt{(y - 2x + 1)^2 + b}} = 0. \quad (6)$$

The activation energy of the process is given by $E_a = V^-(x_2) - V^-(x_1)$, while the reaction free energy G_0 is given by the difference $V^-(x_3) - V^-(x_1)$.† Using the definition of $\alpha = \frac{dE_a}{dG_0} = \frac{dE_a}{dy} / \frac{dG_0}{dy}$ as well as (5) and (6) we obtain

$$\alpha = \frac{x_2 - x_1}{x_3 - x_1}. \quad (7)$$

†Strictly speaking one also must include the change in vibrational entropy associated with the distortion of the potential-energy surface when calculating E_a and G_0 . The author thanks D. W. Schmickler (University of Bonn) for this remark.

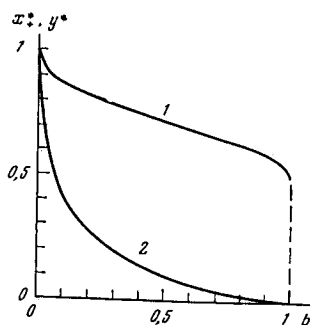


Fig. 2. Functions x_+^* (b) (1) and y^* (b) (2).

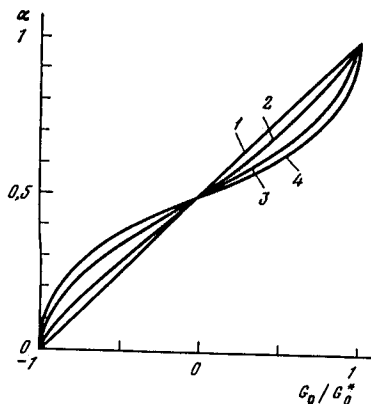


Fig. 3. Function $\alpha(G_0/G_0(y^*))$; the b-values: 1) 0, 2) 0.001, 3) 0.4, and 4) 0.9.

Thus, transfer coefficient α is simply related to the roots of Eq. (6).

One can readily see that for $y = 0$ and $G_0 = 0$, roots x_1 and x_3 of Eq. (6) are related as $x_1 + x_3 = 1$, while $x_2 = 1/2$ and $\alpha = 1/2$. Free energy G_0 increases (decreases), $\alpha(G_0)$ increases (decreases), and roots x_2 and x_3 (x_1 and x_2) come closer with increasing (decreasing) y . For certain values $y = \pm y^*$ and the corresponding values $G_0 = \pm G_0^*$, the roots merge ($x_2 = x_3 = x_+^*$) and $\alpha = 1$ (or $x_1 = x_2 = x_-^*$ and $\alpha = 0$), while surface $V^-(x)$ has a single maximum at $x = x_1$ (or $x = x_3$). The value of y^* can be obtained from (6) while the condition $d^2V/dx^2 = 0$ is satisfied simultaneously:

$$b/[(y-2x+1)^2+b]=1. \quad (8)$$

From (8) and (6) we obtain†

$$y^* = [1-b^{1/2}]^{1/2}, \quad (9)$$

$$x_{\pm}^* = \frac{1 \pm \sqrt{1-b^{1/2}}}{2}. \quad (10)$$

Plots of $y^*(b)$ and $x_+^*(b)$ are shown in Fig. 2. It follows from (9) and (10) that for $b \geq 1$, the potential-energy surface $V^-(x)$ does not have two minima at any value of y .

Thus, the reaction free energy G_0 changes from $-G_0(y^*)$ to $G_0(y^*)$ and transfer coefficient α changes from 0 to 1 when parameter y is varied in the limits of $-y^* < y < y^*$. The results obtained when calculating

†Relation (9) had been obtained previously in [10].

‡In the discussion given in [10], the transfer coefficient α was defined as $dE_a/d\Delta I$. Quantity α thus defined can be written as $\alpha = x_2 - x_1$, and varies in the limits of $0 \leq \alpha \leq x_+^* - x_1(y^*) < 1$. Quantity $(RT/F)d \ln i/d\eta$ resulting from electrochemical experiments (in concentrated solutions where the ψ' -effect can be neglected) in our opinion must be identified with quantity α as defined by (7), in the case of adiabatic processes.

function $\alpha(G_0)$ for a number of values of parameter b are presented in Fig. 3. It follows from the calculations that the behavior of $\alpha(G_0)$ has two special features in adiabatic processes. First, the transfer coefficient changes more slowly than in nonadiabatic reactions at small absolute values of G_0 . Secondly, the transitions to the barrierless region [11] ($\alpha \approx 1$) and to the activationless region ($\alpha \approx 0$) occur more rapidly, in contrast to (1).

We note that to the contrary, transitions to $\alpha = 1$ and $\alpha = 0$ which are smoother than (1) usually are found when excited quantum states of the system are taken into account in calculations of function $\alpha(G_0)$ [12].

Let us now consider the more general case of a system with an arbitrary number of intramolecular degrees of freedom and with multidimensional description of the state of the polar medium. Assuming that the harmonic approximation holds and that the frequencies in the initial and final state remain unchanged we have

$$U_i = \frac{1}{2} \sum_k \hbar \omega_k q_k^2; \quad U_f = \frac{1}{2} \sum_k \hbar \omega_k (q_k - q_{k0})^2 + \Delta I. \quad (11)$$

Here, q_k are the generalized coordinates of the classical degrees of freedom of the solvent and of the intramolecular classical degrees of freedom.

From (4) and (11) and the condition $dV/dq_l = 0$, we obtain a system of equations for the determination of extreme points:

$$\frac{\hbar \omega_l}{2} (2q_l - q_{l0}) + \frac{\left(\Delta I + E_s - \sum_m \hbar \omega_m q_m q_{m0} \right) \frac{\hbar \omega_l}{2} q_{l0}}{\sqrt{\left(\Delta I + E_s - \sum_m \hbar \omega_m q_m q_{m0} \right)^2 + 4L^2}} = 0. \quad (12)$$

With the notation of $\Delta I/E_s \equiv y$ where $E_s = \sum_m E_{sm} = \sum_m \frac{\hbar \omega_m}{2} q_{m0}^2$, $b \equiv 4L^2/E_s^2$, and $x = q_l/q_{l0}$ we obtain

$$y+1 - \sum_m (x_m E_{sm}/E_s) + \frac{2x_l - 1}{\sqrt{\left(y+1 - \sum_m (x_m E_{sm}/E_s) \right)^2 + b}} = 0. \quad (13)$$

It follows from (13) that all x_l coincide, so that (13) changes to (6), and all results obtained above for the one-dimensional case remain valid in the multidimensional case.

The above trends in the behavior of α should be preserved or, in certain cases, become even more distinct when the intramolecular degrees of freedom are described by potentials differing from the harmonic.

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A STUDY OF THE ADSORPTION OF α -NAPHTHOL ON THE MERCURY/n-PROPYL ALCOHOL BOUNDARY

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The adsorption of α -naphthol from propanol solutions is studied by determining the differential capacitance curves of a mercury electrode. It was shown that α -naphthol is not desorbed in the case of positive surface charge as a consequence of π -electron interaction. The orientation of the α -naphthol molecules on the mercury surface depends on the surface charge and on the α -naphthol concentration in solution. The differences in the adsorption tendency of α -naphthol in dimethylformamide and propanol solutions were explained in terms of the extent of interaction of the solvent with the metal surface.

The adsorption of α -naphthol on mercury from aqueous solutions has been studied previously in a number of investigations. Thus, on the basis of the electrocapillary curves (ECC) determined in 0.1 N HCl solutions, Bockris et al. [1] concluded that there was a predominantly planar orientation of α -naphthol on the mercury surface as a result of π -electron interaction. Meibuhr [2] came to a similar conclusion in a study of the dependence of the boundary tension on the potential in the dropping period in 1 N H₂SO₄ solutions with α -naphthol additives. Loshkarev et al. [3] used differential capacitance (background + 1 N H₂SO₄) data for calculating the adsorption parameters of α -naphthol. The complex nature of the dependence of the limiting adsorption on the potential calculated from the ECC indicates orientation of α -naphthol molecules in two positions: 1) a planar position on the positively charged mercury surface and 2) a vertical position for negative charge of the mercury surface. We came to the same conclusion in treating the data obtained by measuring the differential capacitance in the α -naphthol-dimethylformamide (DMF) system [4].

In studying the role of the solvent in the adsorption of organic compounds it was of interest to study the adsorption behavior of α -naphthol on the mercury/n-propyl alcohol boundary. In its physical properties, n-propyl alcohol occupies an intermediate position between water which is a typical protic solvent and DMF which is an aprotic solvent.

In the present work, we compared the results obtained in solutions of propyl alcohol and DMF. We could not use the data obtained by other workers [1-3] in the α -naphthol + HCl or H₂SO₄ + H₂O system since protonation of the unshared electron pair of the α -naphthol hydroxyl group is possible in acid solutions and this may significantly alter the electron density distribution of the aromatic molecule and lead to a change in the extent and mechanism of adsorption.

The adsorption of α -naphthol from 0.1 N LiClO₄ solutions in propyl alcohol was studied by measuring the differential capacitance on a mercury electrode using an R-568 alternating current bridge. All the reagents used were subjected to further purification. Chemically pure grade n-propyl alcohol was heated at reflux over CaO for 5 h and then distilled using a distillation column at atmospheric pressure. The second distillation fraction was used for the work. Lithium perchlorate served as the base electrolyte since it is more soluble in n-propyl alcohol than other neutral electrolytes. A sample of lithium perchlorate was obtained by the neutralization of purified perchloric acid with lithium carbonate. The trihydrate was subjected to prolonged drying in vacuum at 220°C until constant weight. The purity of the salt was monitored by chemical and spectro-

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