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The effect of the electron–electron interaction on the pre-exponential factor of the rate constant of the adiabatic electrochemical electron transfer reaction

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Abstract

It is shown within the simple model of the polar solvent and the classical multidimensional transition state method in the harmonic approximation that the pre-exponential factor of the rate constant of the adiabatic electrochemical electron transfer reaction depends on the energy of the Coulomb repulsion of electrons occupying the valence orbital of the reactant. The exact expressions for the effective frequency ω_{eff} determining the pre-exponential factor are obtained using two exactly solvable limits of the Anderson–Newns model: the surface-molecule model and the wide-bands approximation for the electronic structure of an electrode. The list of expressions for ω_{eff} for different particular cases is presented. It is shown that, due to the non-zero Coulomb repulsion, the transition state method in the harmonic approximation breaks down in some regions of values of physical parameters of the system. The stochastic approach permits the proper calculations of ω_{eff} in this case. The results of calculations of ω_{eff} are presented and the effect of the Coulomb repulsion on the dependencies of ω_{eff} on the electronic matrix element and the overvoltage are studied. It is shown that this effect can be rather significant.
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Keywords: Electron transfer; Adiabatic electrode processes; Pre-exponential factor; Anderson model; Coulomb interaction

1. Introduction

It is well known [1] that two important limiting cases can be considered for the electrochemical electron transfer reactions: the non-adiabatic electron transfer reaction and adiabatic one. The last case is met when the electronic coupling between a redox system (RS) (ion or molecule) and a metal electrode is strong enough. The theory of the adiabatic electrochemical electron transfer reactions with the account of the electron–electron interaction at the valence orbital of RS was presented in Refs. [2–5]. This theory is based on the exactly solvable limits of the Anderson–Newns model and, unlike the other papers on this subject,

takes into account the electron correlation effects exactly. The surface-molecule (SM) limit of the Anderson–Newns model was used in [2] for the study of the adiabatic electron transfer reactions in the case when the electrode is a transition metal. On the contrary, the wide-band approximation is generally assumed for the s–p metals. The exact solution of the Anderson model obtained by the Bethe ansatz method within the wide-band approximation (see, e.g., Refs. [6,7]) was adapted in [3] for the study of the adiabatic electron transfer reactions in the case when the electrode is the s–p metal. The results of [3] were then used for the construction of the kinetic regime diagrams (KRD) and the calculations of the adiabatic Gibbs energy surfaces (AGES) with due account of the electron correlation effects [4,5]. It was shown [2–5] that the electron correlation effects play an important role in the adiabatic electrochemical electron transfer reactions and lead not only to the quantitative

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corrections to the results obtained in the spin-less model or in the Hartree–Fock approximation but also to new qualitative effects.

However, only AGES and activation Gibbs energies were studied and calculated in [2–5]. The problem of the calculations of the pre-exponential factors of the rate constants of the adiabatic electrochemical electron transfer reactions with due account of the electron–electron interaction was not considered. The present paper addresses to this problem.

As in Refs. [2–5], we consider the fluctuations of the solvent polarization in the classical limit and do not take into account the inner sphere reorganization. It is also assumed that the statistical equilibrium exists within the region of the parameters of the slow subsystem lying between the saddle point of AGES and the initial state of the reaction. Then the electron transition probability per unit time from the initial to the final state for the adiabatic electron transfer reaction in the classical multidimensional transition state method with the use of the harmonic approximation for AGES at the initial and transition states has the form [8–10]:

$$W_{\text{adi}\to\text{f}} = \frac{\omega_{\text{eff}}}{2\pi} \exp(-E_a/k_{\text{B}}T), \tag{1}$$

where the activation Gibbs energy E_a is determined by the saddle point on AGES, k_{B} is the Boltzmann constant, T is the temperature and the effective frequency ω_{eff} is given by

$$\omega_{\text{eff}} = \frac{k_{\text{B}}T}{\hbar} \frac{Z^*}{Z_{\text{i}}} = \frac{\prod_{k=1}^{N} \omega_k^{(\text{i})}}{\prod_{k=1}^{N-1} \omega_k^*}. \tag{2}$$

Here, Z^* and Z_{i} are the statistical sums of the transition and initial states, respectively. ω_k^* and $\omega_k^{(\text{i})}$ are the frequencies of the effective oscillators in these states and will be defined later, N is the number of the degrees of freedom of the classical subsystem. It should be noted that the statistical sum Z^* includes only the frequencies corresponding to the solvent coordinates along the potential barrier so that the frequency corresponding to the solvent coordinate perpendicular to the barrier is omitted. If one substitute $\omega_k^{(\text{f})}$ for $\omega_k^{(\text{i})}$ in the right-hand side of Eq. (2), the expression for the effective frequency for the transition from the final to the initial state will be obtained.

The expression for the pre-exponential factor of the rate constant of the adiabatic electrochemical electron transfer reactions can also been obtained using the stochastic approach [11–13]. Retaining the same notions as in Eq. (1), we write ω_{eff} in the form [12,13]

$$\omega_{\text{eff}} = \frac{\omega_{\text{i}} E_{\text{r}} (8\pi k_{\text{B}}T)^{1/2}}{\tau_{\text{L}}} \left\{ \int_{E_{\text{i}}}^{E_{\text{f}}} \exp\left[\frac{U_{ad}(E) - U_{ad}(E_t)}{k_{\text{B}}T}\right] \text{d}E \right\}^{-1}, \tag{3}$$

where $U_{ad}(E)$ is the double-well one-dimensional AGES depending on the energy variable E, $\omega_{\text{i}} = (\partial^2 U_{ad}(E_{\text{i}})/\partial E^2)^{1/2} \approx (2E_{\text{r}})^{-1/2}$ is the frequency in the initial state of the electron transfer reaction, E_{r} is the reorganization Gibbs

energy, E_{i} and E_{t} are the coordinates of the initial and transition state, respectively, and τ_{L} is the longitudinal relaxation time.

The problem of the calculation of ω_{eff} for the charge transfer reactions in the polar solvents was considered using both stochastic approach [12,13] and the classical multidimensional transition state method [14,15] (see also Ref. [16] where the comprehensive review of both methods is presented) under the condition that the electronic subsystem consists of a single electron.

Eq. (3) was obtained under the conditions that $E_a \gg k_{\text{B}}T$ and the friction coefficient is large enough so that the stochastic approach is considered below only in the large friction limit. It should be noted that, in the small friction limit, the expression for the pre-exponential factor produced by the one-dimensional stochastic method reduces to the one-dimensional transition state method result (see, e.g., Eqs. (25) and (26) of Ref. [11]). However, if one considers the multidimensional system and introduces AGES $U_{ad}(E)$ depending on the single effective coordinate E, the degree of freedom E couples strongly to other degrees of freedom of the system as is discussed in the present paper. Therefore, it can be suggested that, for some cases, the multidimensional transition state method is equivalent to the stochastic approach in its large friction limit. This problem was studied in [14,15]. It was shown that both methods give the same result for ω_{eff} when the electronic subsystem consists of a single electron, the Debye model is used for the approximation of the frequency-dependent dielectric function $\varepsilon(\omega)$ of the solvent and both the double-well one-dimensional AGES of the stochastic approach and the multidimensional AGES are considered in the harmonic approximation at the points of interest. In this case the expression for ω_{eff} takes the form [15]:

$$\omega_{\text{eff}} = \{[(E_{\text{r}}/2C) - 1][1 - (E_{\text{r}}/2C_i)]\}^{1/2}/\tau_{\text{L}}, \tag{4}$$

where C and C_i are functions of V, E_{r} and ΔF, V is the absolute value of the electronic matrix element and ΔF is the Gibbs energy of the transition. For example, $C = V$ and $C_i = E_{\text{r}}^3/8V^2$ for $\Delta F = 0$ and $V \ll E_{\text{r}}$. The exact expressions for C and C_{i} for the spin-less two-site model are presented below. It follows from Eq. (4) that the pre-exponential factor of the rate constant depends on V, E_{r} and ΔF [10,12–15].

AGES for the single electron subsystem considered in [12–15] are identical to those in the spin-less two-site model of Hush (see Ref. [17]). The spin-less two-site model for the electronic subsystem can be used in the case of the electron transfer reaction in the bulk of the solvent when only one valence electron is presented in the electronic subsystem. The Hush generalization of the spin-less two-site model to the electrochemical electron transfer reactions consists in the replacement of the electronic states of the metal electrode by a single effective electronic orbital [2]. However, due to the multielectron character of the whole system,