

الانتقال الالكتروني عند سطوح شبه الموصل / سائل

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الخلاصة

ثابت معدل الانتقال للتفاعل الالكتروني داخل سطوح شبه الموصل / سائل حسب استخدام قاعدة فيرمي الذهبية لشبه الموصل . طاقة اعادة الالتحام $\lambda(eV)$ حسب السطوح الفاصلة لنظام شبه الموصل / سائل ولمذيين مختلفين وقورنت مع القيم العملية . الطاقة الحرة حسب اعتمادا" على طيف $(NCS)_2$ $Ru(H_2L^`)_2$. الانتقال عومل وفقا" للازدواج الضعيف غير الكظيم لحالتي مستويين بين شبه الموصل وحالة الجزيئات المستقبلة .

Electron Transfer At Semiconductor / Liquid Interfaces

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Abstract

Electron Transfer reaction rate constants at Semiconductor / Liquid interfaces are calculated by using the Fermi Golden Rule for Semiconductor. The reorganization energy $\lambda(eV)$ is computed for Semiconductor / Liquid Interfaces system in two solvents and compared with experimental value. The driving force (free energy) $\Delta G_0(eV)$ is calculated depending on spectrum $Ru(H_2L')_2(NCS)_2$. The transfer is treated according with weak coupling (nonadiabatic) for two – state level between the Semiconductor and acceptor molecule state.

Introduction

Insight into the dynamics of the electron transfer reactions at Semiconductor / liquid interfaces can be helpful in constructing efficient and stable photo electrochemical cells and other applications, and is of interest in understanding the basic chemical reactions (1). Due to the instability and the nonideal behaviour of most Semiconductor electrodes in contact with liquids, only recently we have reliable kinetic measurements been performed at Semiconductor electrolyte interfaces (2).

Photo emission (3) involves the excitation of electrons from the valence band of the Semiconductor to the conduction band, the diffusion of the excited electrons toward the surface, and their emission into Vacuum. Photo electrochemical transfer (emission) of electron at the Semiconductor / liquid interfaces involves similar processes except that the photo electrons undergo a transition through the interfacial barrier to the acceptor state in the solution (4). The energy band diagrams of an n - type Semiconductor and a p – type Semiconductor in contact with a liquid are shown in figure (1) (5), before and after the equilibration of the Fermi levels together with the charge carrier profiles for electrons. The equilibration processes at Semiconductor / liquid interface involving either n – type or p – type electrodes are so closely related that the description will be restricted to the case of an n – type Semiconductor charge – transfer processes in electrodes separated by less than 1 nanometer (5). In the present paper, the electron transfer reactions at Semiconductor / liquid interfaces nonadiabatically. The procedure is applied to TiO_2 Semiconductor / Ruthenium complex liquid interfaces.

Theoretical Model

The rate of a nonadiabatic electron tunneling from one electronic state to another is frequently described by the Landau – Zener formula (6). Under the weak – coupling assumption, the Golden Rule expression for the nonadiabatic electron transfer rate constant, which includes both the electron tunneling and the "nuclear reorganization energy", contains implicitly the Landau – Zener expression (7).

$$K = \frac{2\pi}{\hbar} |V|^2 FC \dots\dots\dots [1]$$

Where FC is the Franck – Condon factor, V is the electronic coupling matrix element, and \hbar is Plancks constant. A common classical expression for the Franck – Condon factor is (7-8).

$$FC = \frac{1}{\sqrt{4\pi\lambda K_B T}} \ell^{\left[\frac{-(\lambda+\Delta G)^2}{4\lambda K_B T} \right]} \dots\dots\dots [2]$$

Where λ is the reorganization energy, and ΔG is a free energy of reaction under the prevailing conditions of temperature, electrode – solution potential difference and environment. When the electron transfer at the Semiconductor / liquid interfaces involves the continuum of electronic states in the donor or acceptor levels for the Semiconductor / liquid system, the right – hand side of equ. [1] is integrated appropriately over these levels. The rate constant for electron transfer can then be written as (9).

$$K = \frac{2\pi}{\hbar} \frac{1}{\sqrt{(4\pi\lambda K_B T)}} \frac{V}{\beta} \int \ell^{\frac{-(\lambda+\Delta G)^2}{4\lambda K_B T}} |V_{(E)}|^2 f_{(E)} d_{(E)} \dots\dots\dots [3]$$

Where V is the volume of the unit cell in the Semiconductor, β is the exponent for the decay of the square of the matrix element with distance and $f_{(E)}$ is the Fermi – Dirac distribution. The probability that a state in the Semiconductor with energy E is occupied. The occupancy of these states obey the Fermi – Dirac distribution (10).

$$f_{(E)} = \frac{1}{1 + \ell^{\left[\frac{(E-E_f)}{K_B T} \right]}} \dots\dots\dots [4]$$

Where $E_{(f)}$ is the Fermi level. The driving force for the electron transfer from a surface state with energy E to the acceptor is related by (2).

$$\Delta G = \Delta G_o - E \dots\dots\dots [5]$$

Here, ΔG_o is defined as the standard free energy of the reaction when the donor state in the electrode is at the conduction band edge at the Semiconductor surface. ΔG_o can be obtained from electrochemical measurements or theoretically by using the relation (7-8).

$$h\nu = \lambda + \Delta G_{\circ} \dots\dots\dots [6]$$

Where h is the planck constant, and ν is the frequency of the spectral absorption. The reorganization energy. λ is defined as the energy which is required for the structural reorganizing of the donor, acceptor, and their salvation spheres upon electron transfer (11). The theoretical reorganization energies values may be estimated based on continuum, the reorganization energy λ for redox active ions at semi conducting is (11).

$$\lambda = \frac{1}{2} \frac{q^2}{4\pi\epsilon_{\circ}} \left[\frac{1}{D} \left(\frac{1}{n^2} - \frac{1}{\epsilon} \right) - \frac{1}{2R} \left(\frac{n_{se} - n^2}{n_{se}^2 + n^2} \cdot \frac{1}{n^2} - \frac{\epsilon_{se}^2 - \epsilon^2}{\epsilon_{se}^2 + \epsilon^2} \cdot \frac{1}{\epsilon^2} \right) \right] \dots\dots\dots [7]$$

Here ϵ_{\circ} is the vacuum permittivity, q is the electronic charge, ϵ is the static dielectric constant of the solvent, n is the refractive index of the solvent, R is the distance between the Semiconductor and the molecule in the solvent, D is the radius of the molecule, n_{se} is the refractive index of the Semiconductor and ϵ_{se} is the dielectric constant of the Semiconductor. In the case of electron transfer from a Semiconductor to a reactant species in the solution, the rate is the first order in the concentration of the electron in the Semiconductor at the surface and the first order in the reactant. By substituting equations [4] and [5] in equation [3] we get an expression for the nonadiabatic rate constant K_{ET} which was given earlier (9).

$$K_{ET} = \frac{2\pi}{\hbar} \frac{V}{\sqrt{4\pi\lambda K_B T}} \frac{1}{\beta} \int_0^{\infty} e^{\left[\frac{-(\lambda + \Delta G_{\circ} - E)^2}{4\lambda K_B T} \right]} \left\langle \left| V_{(E)} \right|^2 \right\rangle f_{(E)} \rho_{(E)} dE \dots\dots\dots [8]$$

Where $\rho_{(E)}$ is the density of states and $\left\langle \left| V_{(E)} \right|^2 \right\rangle$ is the averaged quantity of coupling matrix element, $\rho_{(E)}$ and $\left\langle \left| V_{(E)} \right|^2 \right\rangle$ are normalized to the unit cell. For a Semiconductor /electrolyte interface as in the electron transfer reaction studies in (2), the change of electrostatic potential across a Semiconductor / liquid interface exists mainly within the Semiconductor, because of the low concentration of the charge carriers in the Semiconductor. In this case, the change of the applied potential changes only the concentration of carriers at the interface and does not change the free energy ΔG_{\circ} of the electron transfer reaction. The electron transfer rate constant can then be expressed as (2, 9).

$$K_{ET} = \frac{2\pi}{\hbar} \frac{1}{\sqrt{4\pi\lambda K_B T}} \frac{V}{\beta} \langle |V|^2 \rangle \dots\dots\dots [9]$$

Where

$$\langle |V|^2 \rangle = \frac{\int_0^\infty \langle |V_{(E)}|^2 \rangle f_{(E)} \rho_{(E)} dE}{\int_0^\infty f_{(E)} \rho_{(E)} dE} \dots\dots\dots [10]$$

is the coupling between the Semiconductor and the redox molecules which was not calculated for an actual system because the calculation of $|V|^2$ is very difficult .

Results

According to the rate constant expression [9], for electron transfer in Semiconductor / liquid interface, we have first done the calculations of the reorganization energies $\lambda(eV)$ by using equation [7] for $TiO_2/ Ru(H_2L^*)_2 (NCS)_2$ interface in 1-Butanol and acetonitrile solvent where ϵ and n are the static dielectric constant and refractive index for solvents which are presented in table (1), D is the radius of the molecule $D=3.5 \text{ \AA}$ (12), R is the distance between

the complex and the electrode $R = D + 1 \text{ \AA}$ (5), n_{se} and ϵ_{se} are the refractive index and dielectric constant. We can compute the reorganization energy $\lambda(eV)$ by inserting

the values $D = 3.5 \text{ \AA}$ (12), $R = 4.5 \text{ \AA}$ (5), $\epsilon_{se} = 86$ (11), $n_{se} = 2.5$ (11), n and

ϵ from table (1) in equation [7], noting that $e^2 / 8\pi\epsilon_0 \approx 7.2eV$, and these results were summarized in table (1). Next, the other important factor for electron transfer rate constant is the free energy (driving force energy) $\Delta G_0(eV)$ for $TiO_2/ Ru(H_2L^*)_2 (NCS)_2$ interface in solvents which may be calculated from equation [6], where $h\nu = hc / \text{wave length}$, h is Planck's constant, c light velocity, and wave length in nanometer which is taken from absorption spectra of $Ru(H_2L^*)_2(NCS)_2$ (400 - 850) nm (13). The values of $\Delta G_0(eV)$ which are calculated by using two solvents are summarized in table (2). The most important factors controlling the rate of electron transfer are the electronic coupling term $|V|^2$ that were defined in equation [10]. In this work the values of coupling coefficients are ($3 \times 10^3 \text{ cm}^{-1}$) which were taken from Mulliken Hush equation [14]. Other parameters used in

this calculation as the volume of the until cell was the calculation by using $V = a^3 = 2(r_{o_2} + r_{Ti})/\sqrt{3} \approx 2.947 \times 10^{-23} \text{ cm}^3$ where $r_{o_2} = 0.06 \text{ nm}$ and $r_{Ti} = 0.1475 \text{ nm}$ are radius of oxygen and Titanium respectively (15), and the decay exponent β typically by using $\beta \approx 1 \text{ \AA}^{-1}$ (2). Finally, we can calculate the rate constant of the electron transfer for the Semiconductor / liquid in the solvent system by substituting the results of $\lambda(\text{eV})$, $\Delta G_o(\text{eV})$, $|V|^2(\text{eV})$, $V(\text{m}^3)$, $\beta(\text{m}^{-1})$ in equation [9], the results are listed in table (3).

Discussion

The nonadiabatic description and the two – state level approximation applied in our theoretical studies of electron transfer reaction at semiconductor / liquid interfaces provide a constant values for the reaction rate constant. Semiconductors differ from metals because of their band gap which makes the electron transfer reaction more likely to be nonadiabatic. This effect is associated with the low occupancy of the semiconductor conduction band, which allows the electron transfer to occur, mainly near the conduction band. Rate constant of this transfer is dependent on many factors, one of them is the reorganization energy $\lambda(\text{eV})$. The results of our calculations in two solvents table (1), show that there is a large value for a more solvent $\lambda \approx 0.844 \text{ eV}$ for acetonitrile compared with $\lambda \approx 0.726 \text{ eV}$ for 1-Butanol This dependent is on the polarity of the solvent (have a large dielectric constant $\epsilon = 37.5$ for the acetonitrile compared with $\epsilon = 17.8$ for 1- Butanol), this leads to a high reorientation of the molecule the about electrode the Value of reorganization energy for the acetonitrile $\lambda = 0.844 \text{ eV}$ is in a very good agreement with the experimental Value $\lambda = 0.83 \pm 0.05 \text{ eV}$ for acetonitrile (11). The free energy $\Delta G_o(\text{eV})$ is to take to the injected electrons recombined from the conduction band or from trap states with the oxidized sensitizer ΔG_o values are calculated depending on the absorption spectra. All results of $\Delta G_o(\text{eV})$ are negative, this indicates the free energy which is apart of the work can be broken into the recombination of the electrons in semiconductor / liquid interface. Value of $\Delta G_o \approx -1.406 \text{ eV}$ for acetonitrile at 550 nm fits the with experiment value $\Delta G_o \approx -1.45 \text{ eV}$ at the same solvent. The difference between the calculated results for electron transfer rate constant for $\text{TiO}_2/\text{Ru}(\text{H}_2\text{L}')_2(\text{NCS})_2$ system in two solvents may be due to several effects : one factor is the polarity of the solvent, this effect would yield a large reorganizing energy. However there are factors which make TiO_2 more effective, e.g, large electronic coupling between the semiconductor and redox molecule. We have compared the calculated rate constant for semiconductor / liquid system in 1- Butanol as in table (2). with a rate constant which we have subsequently calculated for $\text{TiO}_2/\text{Ru}(\text{H}_2\text{L}')_2(\text{NCS})_2$ in acetonitrile. Thus it is seen that the K_{ET} for $\text{TiO}_2/\text{Ru}(\text{H}_2\text{L}')_2(\text{NCS})_2$ in acetonitrile has higher rate than in 1- Butanol solvent, this indicateds that K_{ET} depends on the dielectric constant, viscosity, radius, and the density of electron at the electrode to all the acceptors in the solvent. Another important parameter is the coupling matrix element of the wave function between a solid electronic state and the acceptor state.

Conclusions

Electron transfer was studied in titanium dioxide electrodes sensitized with the ruthenium polypyridyl complex $\text{Ru}(\text{H}_2\text{L}^-)_2(\text{NCS})_2$ with was chosen as the electron acceptor. The $\lambda(eV)$ values for the semiconductor / liquid interface in acetonitrile solvent is larger than in 1- Butanol solvent. In summary, it can be concluded from the present results of the rate constant for electron transfer K_{ET} with would increase when the solvent is more polar and high dielectric constant, also K_{ET} increases with the decrease of $\Delta G_0(eV)$ for two solvents. From this study we can conclusion an analogous expression can also be written for hole transfer from the valence band of the semiconductor. Also, when it is assumed that the electron transfer from the electrode to the acceptors is proportional to the concentration of the electron at the electrode surface. In accordance with a weak coupling (nonadiabatic) approximation transition can be treated as being occurred between pairs of states and two - state-level approximation with can then be considered, in which the electron transfers between the electrode and an acceptor state.

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Table (1): The reorganization energy $\lambda(eV)$ for [4, 4'-dicarboxylic acid 2,2-bipyridine] Ruthenium complex and Titanium Dioxide semiconductor (TiO_2).

Solvent	Refractive index (n) [16]	Dielectric constant (E) [16]	Reorganization energy $\lambda(eV)$
1- Butanol	1.397	17.8	0.726
Acetonitrile	1.344	37.5	0.844

Table (2): The free energy $\Delta G_0(eV)$ for [4, 4'-dicarboxylic acid 2, 2-bipyridine] Ruthenium complex and Titanium Dioxide semiconductor (TiO_2).

Wave length (nm) [13]	Free energy $\Delta G_0(eV)$ for 1- Butanol	Free energy $\Delta G_0(eV)$ for Acetonitrile
400	2.368	2.25
450	2.024	1.906
500	1.749	1.631
550	1.524	1.406
600	1.337	1.219
650	1.178	1.060
700	1.042	0.924
750	0.924	0.806
800	0.821	0.703
850	0.736	0.612

Table (3): Rate constant K_{ET} of electron transfer between for [4, 4'-dicarboxylic acid 2, 2-bipyridine] Ruthenium complex and Titanium Dioxide (TiO_2) in 1- Butanol and Acetonitrile solvent.

Wave length (nm)	$K_{ET} (m^4 s^{-1})$ in 1- Butanol	$K_{ET} (m^4 s^{-1})$ in Acetonitrile
400	6.053×10^{-40}	5.078×10^{-34}
450	6.791×10^{-34}	1.187×10^{-29}
500	4.468×10^{-30}	4.907×10^{-27}
550	1.262×10^{-27}	1.789×10^{-25}
600	4.756×10^{-26}	1.426×10^{-24}
650	4.879×10^{-25}	4.343×10^{-24}
700	2.057×10^{-24}	6.997×10^{-24}
750	4.742×10^{-24}	7.420×10^{-24}
800	7.186×10^{-24}	5.964×10^{-24}
850	8.135×10^{-24}	3.989×10^{-24}

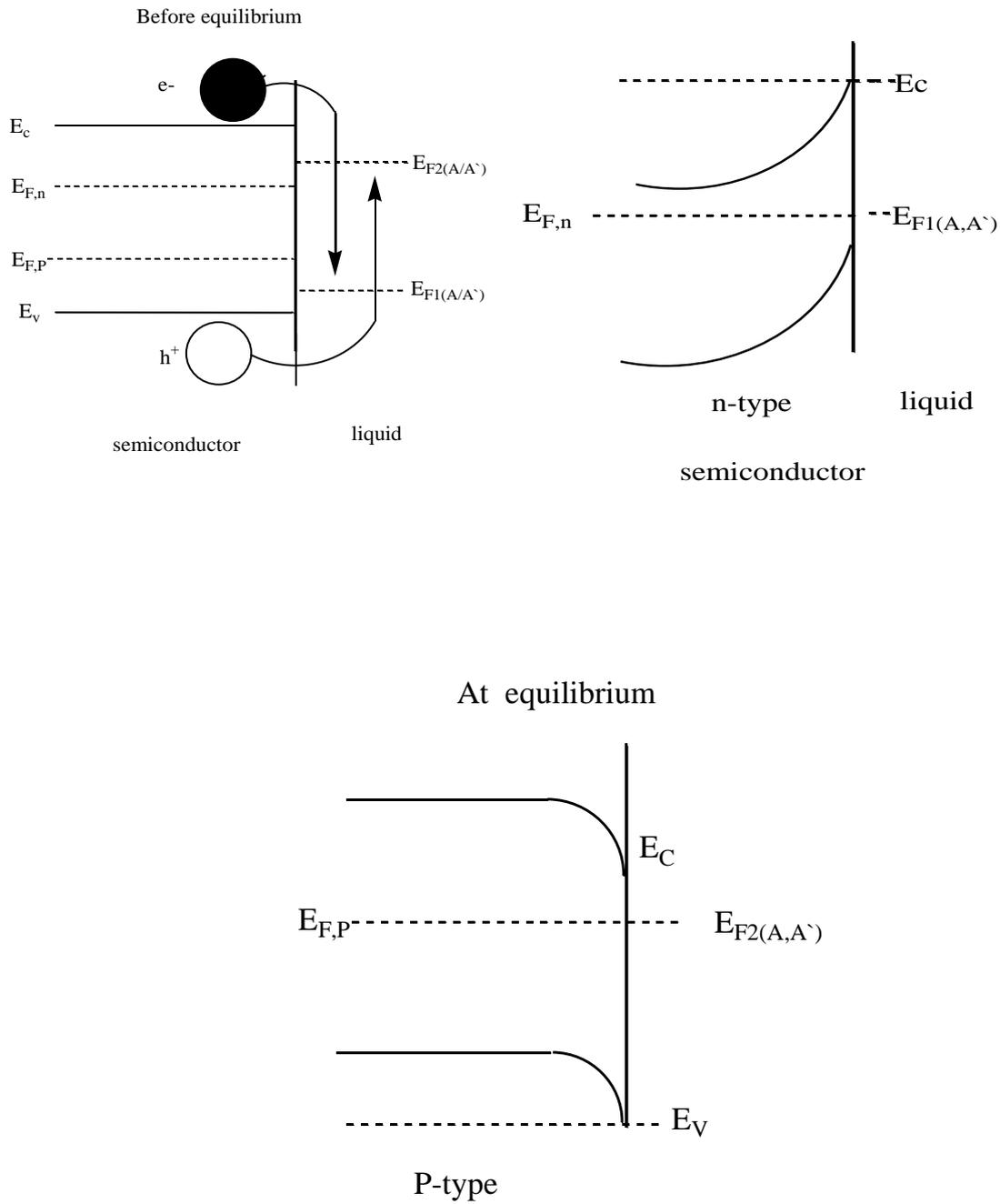


Fig.(1): Band diagram and charge – carrier profiles of n – type and p -type semiconductor / liquid junctions. E_c , E_v , are conduction and valence band energy, E_F is the Fermi energy, e^- , and h^+ are electron and hole respectively [5].