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Electron Transfer between Thionine dye and ZnO Semiconductor in Variety Solvents.

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Abstract

Electron transfer rate constant for dye / semiconductor system has been calculated using Fermi golden rule .The reorganization energy (λ eV) is calculated for this system at three solvents and compared with the theoretical and experimental values. The effective free energy (ΔGo eV) is calculated depending on the spectrum of thionine dye. The transfer is treated according to the weak coupling between semiconductor and acceptor molecule state. Our calculations show good agreement with the theoretical and experimental observed results.

Introduction

Since the late 1940 s , the field of electron transfer was grown enormously, both in chemistry and biology applications. The development of the field, experimentally and theoretically, as well as its relation to the study of other kinds of chemical reactions, represents an intriguing history [1].Electron transfer reactions represent an elementary process which occurs in a large variety molecules, ranging from small ion pairs up to biological systems [2],and plays an important role in a huge number of chemical and biochemistry reactions [2]. Electron transfer usually refers to the transfer of an electron from a localized initial donor state $|D\rangle$ to a localized final acceptor state $|A\rangle$ [3].The dynamics of electron transfer processes is a subject of the experimental and theoretical work. This work deals with intramolecular and intermolecular electron transfer in donor-acceptor [4].The dynamics of electron transfer across semiconductor and dye molecule interfaces were promising for application in solar photo-conversion processes [4].

Electron transfer processes occurring at the dye-sensitized heterojunction, the electron injection was depending on a variety parameters, such as the length between electron donor and acceptor, the density of acceptor states, and the electronic coupling between the dye and semiconductor [5]. Electron transfer at semiconductor - molecule or metal- molecule interfaces is of interest to many research fields [6]. Examples include among others, photocatalysis, surface photochemistry, dye-sensitized solar cells, organic semiconductor based on photovoltaic and nanoscale optoelectronics based on a single molecule or a small group of molecules [6].

The photo-induced electron transfer from the sensitized dye to the semiconductor nanoparticle on which it is chemisorbed is the first key factor of the overall efficiency of dye sensitized solar cells [7].The photo-sensitization of electron transfer a cross semiconductor-solution interface plays an important role in silver halide photography and photovoltaic. Sensitization is achieved by adsorption of dye molecule at the semiconductor surface [8]. Consider an organic light emitting device or field effect transistor (FET), a molecular switch contacted by two metal electrodes, substrate mediated surface photochemistry, and solar energy conversion on dye-sensitized semiconductors. All these processes involve electron transfer between a molecule and semiconductor surface or a metal [9]. In this work the continuum solvent model can be used to calculate the reorganization energy for thionine dye-ZnO semiconductor system.

Theory

The model used is based upon the use of Fermi golden rule to evaluate the rate of process in terms of the value of the matrix element that couples the reactant and product states of the system [10]. In this model the spherical distribution is assumed. The rate constant for nonadiabatic electron transfer between two electronic states D and A is given by [11].

$$K_{et} = \frac{2\pi}{\hbar} H_{DA}^{2} FC \quad \text{..(1)}$$

Where FC is Franck-Condon factor, H_{DA} is the electronic coupling matrix element, which is depending on the electronic wave functions localized on the sites D and A , and $\hbar$ is the reduced Planck's constant($\hbar = \frac{h}{2\pi}$). The Franck-Condon factor which describes the effects associated with nuclear tunneling and thermal active barrier, this factor can be expressed as [12].

$$FC = (4\pi\lambda_{reo}K_{B}T)^{-1/2}\exp\left(-\frac{(\lambda_{reo}+\Delta Go)^{2}}{4\lambda_{reo}K_{B}T}\right) \quad \text{..................(2)}$$

With ΔGo is the free energy, and λ_{reo} is the reorganization energy.

In the case of the electron transfer between the excited dye and semiconductor an expression for nonadiabatic electron transfer rate constant is given by [13].

$$K_{et} = \frac{2\pi}{\hbar}\frac{\nu}{\beta} H_{DA}^{2} \quad (4\pi\lambda_{reo}K_{B}T)^{-1/2}\exp\left(-\frac{(\lambda_{reo}+\Delta Go)^{2}}{4\lambda_{reo}K_{B}T}\right) \text{.............. (3)}$$

Here ν is the volume of the unit cell of the semiconductor, β is the electronic attenuation factor, K_B is the Boltzmann's constant, and T is the temperature.

The reorganization energy λ_{reo} is the energy required to reorganize the system to the optimum configuration for electron transfer and consists of a component associated with donor and acceptor molecules (intramolecular reorganization energy λ_{υ}) and a solvent component (solvent reorganization energy λ_s) [14]. The reorganization energy λ_{reo} for a redox active ions at semiconducting electrode is given by[15].

$$\lambda_{reo}=\frac{e^2}{8\pi\varepsilon_0}\left[\frac{1}{D}\left(\frac{1}{n_{so}^2}-\frac{1}{\varepsilon_{so}}\right)-\frac{1}{2R}\left\{\left(\frac{n_{sem}^2-n_{so}^2}{n_{sem}^2+n_{so}^2}\frac{1}{n_{so}^2}\right)-\left(\frac{\varepsilon_{sem}^2-\varepsilon_{so}^2}{\varepsilon_{sem}^2+\varepsilon_{so}^2}\frac{1}{\varepsilon_{so}^2}\right)\right\}\right] \text{....(4)}$$

Where n_{sem} and n_{so} are the refractive indices of ZnO semiconductor and solvent respectively, ε_{sem} and ε_{so} are the static dielectric constants of ZnO semiconductor and solvent respectively, R is the distance from the acceptor to the semiconductor electrode, D is the radius of the dye molecule, e is the electron charge, and ε_o is the permittivity of the vacuum.

The radius of the dye molecule can be calculated using the following relation [16].

$$\frac{4}{3}\pi D^3 = \frac{M}{N\rho} \qquad \text{.......................................(5)}$$

Where M is the molecular weight of the dye, N is the Avogadro's number, ρ is the density of the dye, and D is the radius of the dye molecule.

The free energy ΔGo is given by [17].

$$h\upsilon^{abs} = \lambda - \Delta Go \qquad \text{..................................(6)}$$

Where $h\upsilon^{abs}$ is the absorption energy which is taken from the absorption spectrum of thionine dye [18].

Results

To determine the electron transfer rate constant theoretically using the expression (3), the calculations are related by many parameters such as the reorganization energy. The reorganization energy λ for the system thionine dye- ZnO semiconductor has been calculated theoretically by using equation (4), one must first calculate the value of the radius of thionine dye from equation (5). Inserting the molecular weight of thionine dye M_{Thi} = 263.75 gm/mol [20]and density ρ = 1.48 gm / cm^3 [20], the value of the radius is D_{Thi} = 4.1

A^o. Inserting the values of refractive index for semiconductor n_{sem} = 1.9 [21], and the static dielectric constant ε_{sem} =8.65 [21], the refractive index and the dielectric constant for solvents are listed in Table(1). These values are inserted in the expression(4), with the value of the dye radius D, and the distance between the molecule dye and the semiconductor R, where R = D +1 [15], the results have been summarized in the Table(1).

Note that $\frac{e^2}{8\pi\varepsilon_o}$ = 7.2 eV. The free energies ΔGo for thionine dye and ZnO semiconductor system are calculated for different solvents by taking the difference between the reorganization energy and the absorption energy $h\upsilon^{abs}$, where $h\upsilon^{abs}$ is the absorption energy, the wavelength is taken from the absorption spectrum (400-800)nm of thionine dye [18]. The important factor that controlling the electron transfer rate constant is the electronic coupling term, H_{DA}, in this work the value of H_{DA} is ($3x10^3$ cm^{-1}) has been taken from the Milliken-Hush equation [22]. Other parameter is used in this calculations is the volume of the unit cell of ZnO semiconductor, which is evaluated from the relation ν = abc for ZnO semiconductor, with a=b= 3.2469 A^o, and c = 5.2069 A^o [23]. The value of the volume of unit cell is ν_{ZnO} = 5.4893 x10^{-23} cm^3, and the value of the electronic attenuation factor is $\beta = 1(A^o)^{-1}$ [24] . Finally we can calculated the electron transfer constant for thionine dye-ZnO semiconductor theoretically in different solvents by substituting the results of λ_{reo} (eV), ΔGo (eV), H_{DA} (eV), ν_{ZnO}(cm^3), and β (cm^{-1}) in the equation (3), the results are listed in Table(3).

Discussion

The goal of the present work is to calculate the reorganization energy λ_{reo}, the driving force ΔGo, and the electron transfer rate constant K_{et} for dye molecules / semiconductor system. The reorganization energy is dependent on the dielectric of the solvents, and increases with increasing its dielectric constant. The reorganization energy is large for more polar solvent and small for less polar solvent, thisindicate that the reorganization energy is dependent on the polarity of the solvent. The reorganization energy for formamide solvent, is one of the polar solvents (ε_o =111) gives small reorganization energy for thionine dye – semiconductor dye as compared with water solvent (ε_o =80),this indicate that the formamide has large refractive index (n_{so} = 1.4475). The values of the reorganization energies are fitting with the experimental values of λ_{reo} = 0.7 eV , λ_{reo} = 0.8 eV [25], λ_{reo} = 0.77 eV , λ_{reo}= 0.83 eV [15] and the theoretical value is λ_{reo} = 0.53 eV [21]. Table(2) shows the results of the driving force(effective free energy), ΔGo (eV), and all these results are negative, this indicate that the effective free energy, ΔGo, is a part of work which can be broken to reorient the donor-acceptor system [26]. The values of ΔGo = -1.43 eV for water, ΔGo = -1.53 eV for formamide, and ΔGo = -1.53 eV for 2-propanol solvent at 550 nm are fitting with experimental value of ΔGo = -1.45 eV, and ΔGo = -1.52 eV [15]. The electron transfer rate constant increases when the solvent is more polar and high dielectric constant, and it increases with increasing the reorganization energy , also the electron transfer increases with decreasing ΔGo (eV) for the solvents.

Conclusions

This work represents the application of the electron transfer theory to calculate the electron transfer rate constant and other parameters for thionine dye- ZnO semiconductor interface system. Electron transfer reaction is studied for interfacial electron transfer from the excited thionine dye molecules to the conduction band of ZnO semiconductor. In this system, the reorganization energy, the effective free energy, and the electron transfer rate constant are calculated for this system at water, formamide, and 2-propanol solvents. The results of electron transfer rate constant increases when the solvent processes high dielectric constant, also the electron transfer rate constant increases with decreasing ΔGo (eV) for the solvents.

Table (1) : The solvent properties and the reorganization energies (λ_{reo}eV) for Thionine dye-ZnO semiconductor system in variety solvents.

Solvent	Refractive index n_{so} [19]	Dielectric constant ε_{so} [19]	Reorganization energy λ_{reo} (eV)
Water	1.333	80	0.831144
Formamide	1.4475	111	0.732807
2-Propanol	1.3772	18.3	0.712787

Table (2): The effective free energies ΔGo(eV) for Thionine dye-ZnO semiconductor system with variety solvents at wavelength (400-800)nm.

Solvent	ΔGo(eV) λ=400nm	ΔGo(eV) λ=500nm	ΔGo(eV) λ=600nm	ΔGo(eV) λ=700nm	ΔGo(eV) λ=800nm
Water	-2.27667	-1.65511	-1.24073	-0.94475	-0.72276
Formamide	-2.37501	-1.75344	-1.33907	-1.04309	-0.82110
2-Propanol	-2.39503	-1.77346	-1.35909	-1.06311	-0.84112

Table(3): Electron transfer rate constant for Thionine dye-ZnO semiconductor system in variety solvents at wavelength(400-800)nm.

Wavelength nm	Water $K_{et}(cm^4 /sec)$	Formamide $K_{et}(cm^4 /sec)$	2-Propanol $K_{et}(cm^4 /sec)$
400	$1.71x10^{-26}$	$1.6x10^{-31}$	$8.75x10^{-33}$
500	$4.01x10^{-19}$	$1.01x10^{-21}$	$2.14x10^{-22}$
600	$1.9x10^{-16}$	$1.00x10^{-17}$	$5.05x10^{-18}$

700	$1.21x10^{-15}$	$4.05x10^{-16}$	$2.73x10^{-16}$
800	$1.23x10^{-15}$	$1.22x10^{-15}$	$1.21x10^{-15}$

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الانتقال الالكتروني بين صبغة الثايونين وشبه الموصل ZnO في مذيبات مختلفة

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الخلاصة

تم حساب ثابت معدل الانتقال الالكتروني لمنظومة صبغة/ شبه موصل باستخدام قاعدة فيرمي الذهبية.طاقة إعادة الترتيب(λ eV) لهذه المنظومة حسبت باستخدام ثلاث مذيبات وقورنت مع القيم النظرية والعملية. الطاقة الحرة الفعالة(ΔGo eV) حسبت اعتمادا على طيف صبغة الثايونين الانتقال عومل وفقا للازدواج الضعيف بين شبه الموصل وحالة الجزيئات المستقبلة. حساباتنا أظهرت تطابقا جيدا مع النتائج النظرية والعملية الملاحظة .