Calculate of the Rate Constant of Electron Transfer in TiO_2 – Safranine Dye System

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Abstract

A theoretical calculations of the rate constant of electron transfer (ET) in a dye – semiconductor system with variety solvent are applied on system contains safranineT dye with TiO_2 in many solvents like water, 1-propanol, Formamide, Acetonitrile and Ethanol.

A matlap program has been written to evaluate many parameters such that, the solvent reorganization energy, effective free energy, activation free energy, coupling matrix element and the rate constant of electron transfer.

The results of the rate constant of electron transfer calculated theoretically are in a good agreement with experimental and theoretical values of other research.

Key Words: electron transfer, dye-semiconductor, quantum mechanical theory

Introduction

Electron transfer (ET) reactions represented a simple process which occurs in donor-acceptor system molecules. The transfer of a single electron from an atom or a molecule to another is considered to be the most elementary chemical and biological reaction. In general, reactions which involve the transfer of an electron are called redox reactions. It should be noted that the particle that is actually transferred in redox reactions need not always be just a single electron. Electron transfer forms the basis of conventional color photography; the absorption of light by an organic dye placed on a small silver halids semiconductor crystal induces the transfer of an electron from the dye to the crystal [1]. Electron transfer can be optically or /and thermally activated and triggers photosynthesis, metabolism, polymerization reactions, electrochemical reaction, etc. Several theories for ET at different levels of sophistication have been developed. The most generally useful theoretical frame work for thinking about electron transfer is Marcus theory [2]. The field of ET has grown enormously since both in the experimental and theoretical sphere. A substantial amount of work had been devoted to the photoinduced ET step in photosynthetic reaction centra of several organisms. Many studies have also been conducted on photoinduced ET in compounds that are much simpler than the active part of biological reaction centra. A relatively new field in which ET plays a role is molecular electronics . This subject has evolved during the 1980's as scientists and technologists have become aware of the potential applications of organic materials. One may think of electrically conducting wires, memories, electronic switches, rectifiers, light –sensitive detectors, electroluminescent device and photoconductors [1].

In our research we have calculated the rate constant of electron transfer in safranine dye with TiO_2 semiconductor system in variety solvent like water, 1-propanol, Formamide, Acetonitrile and Ethanol, by using a theoretical model that derived on this system depending on quantum mechanical and golden rule expression model applied theoretically system with many solvents like water, 1-propanol, Formamide, Acetonitrile and Ethanol.

Theoretical model

The dye should absorb light and upon excitation .This photo excitation of dye leads to well defined change in their redox.

$$Dye + h\nu_f \longrightarrow Dye^* \qquad \text{…………..} (1)$$

Where h is plank constant , ν_f is frequency

Photoexcitation of dye molecules dispersed on the surface of band gap semiconductor, results in ejection of electrons from the excited dye (Dye^*) to the conduction band or energetically accessible surface electronic state of semiconductor.

$$Dye^+ + e_{CB}\ (semiconductor) \xrightarrow{K_{ET}} Dye \qquad \text{…………..} (2)$$

Where the e_{CB} represents the electron ejected from the exited dye molecule to the conduction band. In addition, the dye should be located close to the semiconductor, otherwise luminescence or nonradiative decay takes place instead of electron injection from the excited molecule [3].

A dye couple to semiconductor is an excellent model for processes that occur in the ET fields. The dye should absorb light promotes an electron from the ground state of the dye located in the semiconductor energy gap into an excited state that is in resonance with the conduction band (CB). Typically, the dye excited state is well inside the conduction band [4].

Light excites the dye molecules from the ground state, which is located energetically in the semiconductor band gap, to an excited state resonant with the TiO_2 conduction band, Figure (1) shows the energy level Jobloniske diagram [4].

We have applied the theoretical model that suggested for ET on the dye and metal oxide which are the main focus in this research.

Under this discussion the Hamiltonian of the acceptor /donor system is given by [5]

$$\hat{\boldsymbol{H}} = \hat{H}_D + \hat{H}_A + \hat{H}_{DA} \qquad \text{………………………………………..} (3)$$

This operator obeys the Schrodinger equation [6]

$$i\hbar \frac{\partial}{\partial t}|\psi,t\rangle = \hat{H}|\psi,t\rangle \quad \text{……………….. (4)}$$

The probability of transfer is [7]

$$k_{ET} = \frac{P_n(t)}{t} = \frac{2\pi}{\hbar}|V_{DA}|^2\rho(E) \quad \text{……… (5)}$$

Where $P_n(t)$ is the probability of ET, t is the time , V_{DA} is the Coupling coefficient of ET , $\rho(E)$ is the density of state .

We consider a donor ($|D\rangle$) or acceptor ($|A\rangle$) are a continuum levels the rate constant for ET can then be written as [8]

$$k_{ET} \quad \frac{4\pi^2}{h}\frac{v}{\beta_S}\frac{1}{\sqrt{4\pi\lambda k_B T}}e^{-\frac{(\lambda+\Delta G_o)^2}{4\lambda k_B T}}\int\frac{\langle|V_{(\epsilon,r)}|^2\rangle e^{\frac{-(\epsilon-\epsilon_f)^2}{k_B T}}}{\rho_{(\epsilon)}f_{(\epsilon)}d\epsilon}\rho_{(\epsilon)}d\epsilon \quad \text{…(6)}$$

where, h is Planck constant, λ is reorganization energy, ΔG_o is the effective free energy, k_B is Boltzman constant, T is the absolute temperature, $V_{(\epsilon,r)}$ is Coupling coefficient, $f_{(\epsilon)}$ is Fermi energy, β_S is the decay constant, v is volume of unit cell. The reorganization energy can be derived by treating the solvent as a dielectric continuum and given by [9].

$$\lambda_{\text{out}} = \frac{1}{2}\frac{q^2}{4\pi\epsilon_o}\left[\frac{1}{D}\left(\frac{1}{n^2}-\frac{1}{\epsilon}\right)-\frac{1}{2R}\left(\frac{n_{SC}^2-n^2}{n_{SC}^2+n^2}\frac{1}{n^2}-\frac{\epsilon_{SC}^2-\epsilon^2}{\epsilon_{SC}^2+\epsilon^2}\frac{1}{\epsilon^2}\right)\right] \quad \text{……..(7)}$$

Where ϵ_o is the vacuum permittivity , ϵ is the static dielectric constant of solvent, n is the refractive index of the solvent, n_{SC} is the refractive index of the semiconductor, ϵ_{SC}dielectric constant of the semiconductor, D is the radius of the molecular dye, and R is the distance between the complex and the semiconductor , and *q* is the charge of electron. The radius of the dye molecule can be evaluated from the apparent molar volumes using spherical approach [10].

$$\frac{4}{3}\pi D^3 - \frac{M}{N_A\rho} \quad \text{……………….. (8)}$$

Where M is the molecular weight, N_A is Avogadro number, and ρ is the density.

Where ($\langle|V_{(\epsilon,r)}|^2\rangle$) is an averaged coupling electronic matrix elements square [11]

$$\langle|V_{(\epsilon,r)}|^2\rangle \quad \frac{|V_{(\epsilon,r)}|^2 f_{(\epsilon)}\rho_{(\epsilon)}d\epsilon}{\int f_{(\epsilon)}\rho_{(\epsilon)}d\epsilon} \quad \text{………… (9)}$$

$$k_{ET} = \frac{4\pi^2}{h}\frac{v}{\beta_S}\frac{1}{\sqrt{4\pi\lambda k_B T}}e^{\frac{(\lambda+\Delta G^{\circ})^2}{4\lambda k_B T}}\langle|V_{(\varepsilon,r)}|^2\rangle \qquad \text{.................. (10)}$$

Where ΔG° effective free energy is given by[7]

$$h\nu_f - \lambda - \Delta G^{\circ} \qquad \text{...................... (11)}$$

The volume of unit cell for semiconductor v is given by [12]

$$v \quad abc \qquad \text{……………… (12)}$$

Where a, b, and c are lattice constant of semiconductor.

The coupling electronic matrix elements can be evaluated by the expression [13]:

$$\mathcal{H}_{DA} - H_{DA}\sqrt{\frac{l_{sc}}{d_{sc}^{2/3}(\frac{6}{\pi})^{-1/3}}} \qquad \text{………… (13)}$$

Where l_{sc} is the effective coupling length, d_{sc} is the density of the atom that contributes to the density of states in the bond of concern, and H_{DA} is the electronic parameter.

The average of the square of the coupling which is then multiplied by the volume to yield the total coupling coefficient that's mean.

$$V_{(\varepsilon,r)} = V_{DA} = \mathcal{H}_{DA}v - H_{DA}\sqrt{\frac{l_{sc}}{d_{sc}^{2/3}(\frac{6}{\pi})^{-1/3}}}\, v \qquad \text{…………… (14)}$$

Results

The ET rate constant is determined theoretically, using quantum mechanical theory and the Golden Rule by many parameters; the value of the reorganization energy of the electron donor (D) and acceptor (A) required upon ET, activation free energy ΔG^{*} , the effective free energy ΔG°, and the coupling coefficient matrix element of ET, V_{DA} between two sites donor and acceptor.One initial we have been evaluated the reorganization energy for the safranineT dye with TiO_2 system by using equation(7)with values of $n_{sc} = 2.488$[14] , $\varepsilon_{sc} - 100$[15], $D = 4.4782\ A^{\circ}$, R=5.4782 , and ϵ, n from table (1),the results tabulated in table(1)

The driving force, $\Delta G^{\circ}(eV)$ that is provided by the absorption of light in Dye–Semiconductor interface system that is shown from equation (11). The values of the free energy ΔG° can be calculated for safranine T, TiO_2 system by taking the difference between the reorganization energy (λ) and the absorption energy, where $h\nu$ is the absorption energy were taken from the absorption spectral of safranine T [16], *h*, Plank constant ($h=6.626\times 10^{-34} J.s$), ν_f is the frequency that equals (= velocity of light / wave length),

wave length of safranine -T is taken from absorption spectra (400–800) nm [14], The results obtained are summarized in table (2).

The electron is transfer occurs when its energy is sufficient to excessed the potential barrier represented by the activation free energy $\Delta G^*(eV)$ that is evaluated by inserting the data of the reorganization λ from table (1)[17] ,and the effective free energy from table (2), in to equation (10), one immediately obtains the values of the activation free energy ΔG^* , the values are listed in table (3), for safranine T– TiO_2system with variety solvent. Another important quantity that can be calculated theoretically is the electronic coupling term, V_{DA} , which describes the overlap integral of the donor and the acceptor state [18].

For the semiconductor –dye system the coupling matrix element coefficient can be calculated by using equation (14). Inserting the values of $d_{sc} = 3\times 10^{-8} cm$ [13], $l_{sc} = 2.77\times 10^{22}\frac{atom}{cm^2}$ [13], and atypical values of (H_{DA}=5, 10, 15, 20 cm^{-1}) that assumes in equations (13)and (14), you can evaluate the value of the coupling coefficient, the results are listed in table (4).

The rate constant of ET is depending on the volume of the unit cell through depending on the number of electron density that is proportional with volume by relation [17]. The volume of unit cell is evaluated from equation (12) for any semiconductor with a= b=4.570 $\mathring{A}$ and c=2.989 $\mathring{A}$ [19]for TiO_2 semiconductor. The results of the volume of unit cell for TiO_2 is $v_{TiO_2} = 6.242\times 10^{-23} cm^3$

substitution of these parameters as data into a designed program to calculate the rate constant of ET through the solution of the theoretical model equation. These parameters have been calculated theoretically with distance β is taken ($1\mathring{A}^{-1}$). A matlab program is written to compute the parameters that's leading to the evaluation of the rate constant of ET in ST– TiO_2 using equation (10), the results are tabulated in tables (4) to (8).

Discussion

The electron transport mechanism in dye –semiconductor has been described in term of a quantum mechanical model to transfer across the tunneling region between dye and semiconductor that is created when the semiconductor is brought to contact with dye. In this region /tunneling, the tail of the wave functions for dye and semiconductor over lap. In order for electron tunneling between dye and semiconductor to occur, the initial and final electronic states should have approximated equal energies that happen when consider the dye–semiconductor system interfaces involves the continuum of electronic states.

According to a fundamental postulate of ET theory, these two states are brought into resonance by fluctuations of polar medium surrounding dye and semiconductor system. This resonance is the transition state of ET reaction.

The transfer matrix element (coupling coefficient) V_{DA}, hence controls the dynamics of transition between the donor and acceptor or dye–semiconductor system and is therefore of our interest, it is this matrix element that inters into the expression for the rate of non adiabatic ET reactions. Hence, the typical of the square values of the coupling coefficient (matrix element) can be expected to be in the range $10^{-6} - 10^{-7}\,(eV)^2$ for such system.

ET rates were determined by electronic coupling matrix element V_{DA} between the dye molecule and conduction band (CB) of the semiconductor, the driving force energy (effective free energy $\Delta G_{0}\,(eV)$, activation free energy $\Delta G^{*}\,(eV)$, volume of the unit cell $v\,(cm^{3})$, and the solvent reorganization energy $\lambda\,(eV)$).

The rate of ET values that calculated theoretically is listed in tables (4) to (8) for ST–TiO_2/ system with variety solvent like Water, 1– Propanol, Formamide, Acetonitrile, and Ethanol.

From these results ET occurs in system with most polar solvents like water and Acetonitrile. The solvent reorganization energy are large for more polar solvents and small values for less polar solvents, this indicates that the reorganization energy is dependent on the polarity of the solvents. The values of the solvent reorganization energy that were calculated theoretically were fitting the experimental value $\lambda = 0.7\ eV and\ 0.8\ eV$ [18], and $\lambda = 0.5\ eV$ [20].

The rate constant value that is calculated shows large values for dye –semiconductor system with most polar solvent and high value for safranine T–semiconductor system, this indicates that the ST dye is more reactive towards semiconductor than coumarin dye and ET occurs activity with polar solvents. Table (9) shows the results of rate constant which are in a good agreement with the experimental value rate constant .

Conclusion

In summary, it can be concluded from the present results that.

I– theoretical model was suggested for ET in dye –semiconductor interface provides an excellent model for studying the transfer of electron through the results of this model as fitting with experimental value.

II–The reactions of ET strongly depends on the solvent polarity. For more polar solvents, the reorganization energies are large and small values for less polar solvents, this indicates that, the reorganization energy dependent on polarity of the solvent.

III– The rate constant of ET is large in (dye –semiconductor) system with solvent more polar than less polar.

IV– The rate constant of ET is large in safranine T– semiconductor ,this indicates the safranine T dye is more reactive towards semiconductor .

Reference

1- Wibren,Du.,W.and Gispen.W. H. (2002), Electron transfer in donor–bridge–acceptor system and derived materials, Ph. D. thesis , Debye Institute and university of Utrecht.

2- Franzen , S.; Goldstein, R. F. and Boxer , S. G. (1993), Distance dependence of ET reactions in organized systems: the role of superchange and non-Condon effects in photosynthetic reaction centers " J. Phys. Chem. 97, 3040-3053.

3- Karin,W. (2001), Dye /semiconductor interface ,Ph. D. thesis, Acta university, Uppsala.

4- Walter, R.; Duncan, and Oleg, V. P., (2007), Theoretical Studies of Photoinduced Electron Transfer in Dye-Sensitized TiO2, Annu. Rev. Phys. Chem. 58:143–84.

5- Natalya, A.Z.(2000) Low temperature electronic transport through macromolecules and characteristics of intramolecular electron transfer Department of physics city college of Cuny, New York.

6- Lewiss ,G., (1999), quantum mechanics", Book,wiley.

7- Mohsin ,A. H.(2010) A Quantum Mechanical Model for Electron Transfer at Semiconductor / Dye Interface at Solvent , Thesis, College of Education Ibn AL– Haithem of Baghdad University.

8- Shachi, S. Gosavi. (2003), Electron Transfer at Metal Surfaces, Ph.D Thesis, California Institute of Technology Pasadena, California.

9- Kuciunskas , et al . (2001),J. Phys.Chem. B, 105, 2.

10- René .M., W., (1996)"introduction to electron transfer" PhD Thesis, Amsterdam .

11- Lewis, N. S. (1998), Progress in Understanding Electron-Transfer Reactions at semiconductor liquid interface". J.phys. chem.B. 102(23): 4843.

12- Charles. K. (2005) Introduction to solid state physics" . 8^{TH} , Wiley and Sons INC,

13- Dennis,A;Gaal. James,E.M. Fang, L.; Janie,E.C., and Joseph.T.H., (2004), Nonadiabatic electron transfer at the nanoscale tin-oxide semiconductor/aqueous solution interface , Photochem.photo boil. Scil, 3, 240-245.

14- Pradyot, P. (2003,) Handbook of inorganic chemicals, 938-944, New York.

15- Zhiyong, F. and Jia, G. (2005), Zinc Oxide Nanostructures: Synthesis and Properties" University of California, Irvine, CA 92697, USA, 1-25.

16- Narjess, Z.; Amor, H. and Mahmoud ,D. (2008), Removal of the dye safranineT in the wastewater using mi cellar enhanced ultrafiltration. " Desalination, 222: 348–356.

17- Shafiqul, D.M. I.; Mamoru, F. and Osamu, I.; (1999)," Photochemical reactions of triplet state of safranine-T studied by transient absorption spectroscopy in visible/near-IR regions" Phys. Chem. 1: 3737–3742.

18- Gao,Y.B. and Marcus,R. A. (2000), On the theory of electron transfer at semiconductor/liquid interfaces II: a free electron model, Y. Q. Gao and R. A. Marcus, J. Chem. Phys. 113, 6351 (2000). J. Chem. 113(15).

19- ZHAO, J. WANG, G.; LIANG, Y.; (2008),CHIN.PHYS.LETT 25(12): 4356–4359

20- Gao,Y. Q.; Georgievskii, Y.; and Marcus, R. A.;(2000) on the theory of electron transfers reaction at semiconductor electrode/ liquid interface" J. chem. Phys., 112(7).

21- Fajardo,A.M. and Lewis,N.S. (1997), Free-energy dependence of electron-transfer rate constants at Si/liquid interfaces ,J.Phys.Chem. B 101: 11136.

22- Pomykal, K.E. and Lewis., N.S. (1997), Measurement of Interfacial Charge-Transfer Rate Constants at n-Type InP/CH_3OH Junctions" J.Phys.Chem..B, 101, 2476.

Table (1): the reorganization energies value for donor ST dye and acceptor semiconductor TiO_2

Solvent	Chemical Formula	ε [14]	*n* [14]	*(Our resoult)*λ(eV) for TiO_2
Water	H_2O	80	1.333	0.6798942561
1-propanol	C_3H_8O	20.33	1.3856	0.5795911754
Formamide	$HCONH_2$	111	1.4475	0.5978483206
Acetonitrile	C_2H_3N	37.5	1.3441	0.6480338344
Ethanol	C_2H_6O	24.5	1.3614	0.6116580688

Table (2): the effective free energy $\Delta G_o (eV)$ for safranine T–TiO_2 system with variety solvent at wave length (λ) (400–800)nm

SOLVENT	ΔG_o for $\lambda = 400nm$	ΔG_o for $\lambda = 500nm$	ΔG_o for $\lambda = 600nm$	ΔG_o for $\lambda = 700nm$	ΔG_o for $\lambda = 800nm$
Water	-2.4221656689	-1.8017536839	-1.3881456939	-1.0927114153	- 0.8711357064
1-propanol	-2.5224687496	-1.9020567645	-1.4884487745	-1.1930144959	- 0.9714387870
Formamide	-2.5042116044	-1.8837996194	-1.4701916294	-1.174757350	- 0.9531816419
Acetonitrile	-2.4540260906	-1.8336141056	-1.4200061156	-1.1245718370	- 0.9029961281
Ethanol	-2.4904018562	-1.8699898712	-1.4563818812	-1.1609476026	- 0.9393718937

Table (3): The activation free energy $\Delta G^* (eV)$ for safranine T–TiO_2 system with variety solvents at wave length (λ) (400–800)nm

SOLVENT	ΔG_o for $\lambda = 400nm$	ΔG_o for $\lambda = 500nm$	ΔG_o for $\lambda = 600nm$	ΔG_o for $\lambda = 700nm$	ΔG_o for $\lambda = 800nm$
water	1.11616977517	0.46278100030	0.18444783679	0.062663423547	0.013448154614
1-propanol	1.62820511577	0.75437450925	0.35629516559	0.162307582500	0.066229679289
Formamide	1.51970861371	0.69150932018	0.31821735641	0.139175781600	0.052798412612
Acetonitrile	1.258270732310	0.54225586105	0.22990358346	0.087606717384	0.025078077622
Ethanol	1.442668052168	0.64717487014	0.29164918917	0.123320122540	0.043895583380

Table (4): The coupling coefficient value that is calculated for semiconductor dye system

V_{DA} (cm^{-1})	V_{DA} (eV)	H_{DA} (cm^{-1})	$V_{DA}(eV\ cm^{\frac{3}{2}})$	$V_{DA}^{2}(eV)^{2}$
V_{DA1} −3.25244	$4.032421511*10^{-4}$	5	$V_1=3.18586082*10^{-15}$	$1.626042324*10^{-7}$
V_{DA2} −6.50486	$8.064824289*10^{-4}$	10	$V_2=6.371721642*10^{-15}$	$6.504139082*10^{-7}$
V_{DA3} −9.75730	$1.209723643*10^{-3}$	15	$V_3=9.557582465*10^{-15}$	$1.463431293*10^{-6}$
V_{DA4} −13	$1.612964833*10^{-3}$	20	$V_4=1.274344329*10^{-14}$	$2.601655551*10^{-6}$

Table (5): The rate constant of electron transfer at Safranine T–TiO_2 system with variety solvents at coupling coefficient V_{DA} −4.032421511*10 ^{4} eV

Solvent/ λ nm	Water	1-propanol	Formamide	Acetonitrile	Ethanol
400	$8.542250641\times10^{-}$[illegible]	$1.17833068\times10^{-}$[illegible]	$8.898357073\times10^{-}$[illegible]	$2.974730921\times10^{-}$[illegible]	$1.917267125\times10^{-}$[illegible]
500	$1.914687409\times10^{-}$[illegible]	$1.78344521\times10^{-}$[illegible]	$2.170726702\times10^{-}$[illegible]	$8.16394338*10^{-31}$	$1.264196539\times10^{-}$[illegible]
600	$1.30990681\times10^{-}$[illegible]	$1.46759453\times10^{-}$[illegible]	$6.627515407\times10^{-}$[illegible]	$2.177784004\times10^{-}$[illegible]	$1.896392603\times10^{-}$[illegible]
700	$1.709433055\times10^{-}$[illegible]	$3.42944051\times10^{-}$[illegible]	$8.54321766\times10^{-}$[illegible]	$6.45601581\times10^{-}$[illegible]	$1.59958876\times10^{-}$[illegible]
800	$1.224077414\times10^{-}$[illegible]	$1.60531287\times10^{-}$[illegible]	$2.704892721\times10^{-}$[illegible]	$7.866342259\times10^{-}$[illegible]	$3.818116749\times10^{-}$[illegible]

Table (6): The rate constant of electron transfer at Safranine T–TiO_2 system with variety solvents at coupling coefficient V_{DA} –8.064824289*10^{-4} eV

Solvent /λ nm	Water	1-propanol	Formamide	Acetonitrile	Ethanol
400	$3.416884384\times10^{-\text{[illegible]}}$	$4.713300824\times10^{-\text{[illegible]}}$	$3.55932646\times10^{-\text{[illegible]}}$	$1.189886841\times10^{-\text{[illegible]}}$	$7.669038875\times10^{-\text{[illegible]}}$
500	$7.658714059\times10^{-\text{[illegible]}}$	$7.133744944\times10^{-\text{[illegible]}}$	$8.682866877\times10^{-\text{[illegible]}}$	$3.265562184\times10^{-\text{[illegible]}}$	$5.056762667\times10^{-\text{[illegible]}}$
600	$5.239599985\times10^{-\text{[illegible]}}$	$5.870350983\times10^{-\text{[illegible]}}$	$2.650993971\times10^{-\text{[illegible]}}$	$8.71109555\times10^{-\text{[illegible]}}$	$7.585538172\times10^{-\text{[illegible]}}$
700	$6.837700122\times10^{-\text{[illegible]}}$	$1.371769844\times10^{-\text{[illegible]}}$	$3.417271311\times10^{-\text{[illegible]}}$	$2.58237568\times10^{-\text{[illegible]}}$	$6.370325446\times10^{-\text{[illegible]}}$
800	$4.896286913\times10^{-\text{[illegible]}}$	$6.421221659\times10^{-\text{[illegible]}}$	$1.081952113\times10^{-\text{[illegible]}}$	$3.146522287\times10^{-\text{[illegible]}}$	$1.527239605\times10^{-\text{[illegible]}}$

Table (7): The rate constant of electron transfer at Safranine T–TiO_2 system with variety solvents at coupling coefficient V_{DA} –1.209723643*10^{-3} eV

Solvent/ λ nm	Water	1-propanol	Formamide	Acetonitrile	Ethanol
400	$7.68989861\times10^{-\text{[illegible]}}$	$1.06492685\times10^{-\text{[illegible]}}$	$8.008484413\times10^{-\text{[illegible]}}$	$2.677245391\times10^{-\text{[illegible]}}$	$1.725532397\times10^{-\text{[illegible]}}$
500	$1.757168651\times10^{-\text{[illegible]}}$	$1.605092612\times10^{-\text{[illegible]}}$	$1.953645018\times10^{-\text{[illegible]}}$	$7.347514911\times10^{-\text{[illegible]}}$	$1.1377716\times10^{-\text{[illegible]}}$
600	$1.178909996\times10^{-\text{[illegible]}}$	$1.32082891\times10^{-\text{[illegible]}}$	$5.964736343\times10^{-\text{[illegible]}}$	$1.959996498\times10^{-\text{[illegible]}}$	$1.706745414\times10^{-\text{[illegible]}}$
700	$1.538482602\times10^{-\text{[illegible]}}$	$3.086482148\times10^{-\text{[illegible]}}$	$7.688860331\times10^{-\text{[illegible]}}$	$5.8103868\times10^{-\text{[illegible]}}$	$1.433323225\times10^{-\text{[illegible]}}$
800	$1.101664555\times10^{-\text{[illegible]}}$	$1.444774873\times10^{-\text{[illegible]}}$	$2.434392216\times10^{-\text{[illegible]}}$	$7.079675143\times10^{-\text{[illegible]}}$	$3.436289111\times10^{-\text{[illegible]}}$

Table (8): The rate constant of electron transfer at Safranine T–TiO_2 system with variety solvents at coupling coefficient V_{DA} –1.612964833*10^{-3} eV

Solvent/ λ nm	Water	1-propanol	Formamide	Acetonitrile	Ethanol
400	$1.366753711\times10^{-\text{[illegible]}}$	$1.8853271\times10^{-\text{[illegible]}}$	$1.423730539\times10^{-\text{[illegible]}}$	$4.759547215\times10^{-\text{[illegible]}}$	$3.067613054\times10^{-\text{[illegible]}}$
500	$3.063485527\times10^{-\text{[illegible]}}$	$2.853497888\times10^{-\text{[illegible]}}$	$3.473146642\times10^{-\text{[illegible]}}$	$1.306224833\times10^{-\text{[illegible]}}$	$2.022705003\times10^{-\text{[illegible]}}$
600	$2.095839928\times10^{-\text{[illegible]}}$	$2.348140319\times10^{-\text{[illegible]}}$	$1.060397555\times10^{-\text{[illegible]}}$	$3.484438111\times10^{-\text{[illegible]}}$	$3.03443974\times10^{-\text{[illegible]}}$
700	$2.735508000\times10^{-\text{[illegible]}}$	$5.487079205\times10^{-\text{[illegible]}}$	$1.366908481\times10^{-\text{[illegible]}}$	$1.032957582\times10^{-\text{[illegible]}}$	$2.548130099\times10^{-\text{[illegible]}}$
800	$1.958514703\times10^{-\text{[illegible]}}$	$2.568488583\times10^{-\text{[illegible]}}$	$4.327808314\times10^{-\text{[illegible]}}$	$1.258608897\times10^{-\text{[illegible]}}$	$6.108958229\times10^{-\text{[illegible]}}$

Table (9): compared between our results and experimental and theoretical research for dye -semiconductor

System	Theoretical k_{ET}	Experimental k_{ET}
Si/viologen dye	1.3-1.6$\times 10^{16}$ [20]	0.6$\times 10^{16}$ [21]
InP/Me$_2$Fe	0.084-0.086$\times 10^{16}$[20]	1-2$\times 10^{16}$[22]
Si/viologen dye	1.2-1.9$\times 10^{16}$[18]	0.6$\times 10^{16}$[18]
Si/ Me$_2$Fe	0.024-1.7$\times 10^{16}$[18]	1$\times 10^{16}$[18]
InP/Me$_2$Fe	0.017-1.1$\times 10^{16}$[18]	
ST– TiO$_2$	1.2$\times 10^{20}$-3.4$\times 10^{24}$(our result)	
ST– TiO$_2$	1.10166$\times 10^{20}$(our result)	
ST– TiO$_2$	1.53848$\times 10^{21}$(our result)	
ST– TiO$_2$	1.43332$\times 10^{22}$(our result)	
ST– TiO$_2$	3.08648$\times 10^{23}$(our result)	
ST– TiO$_2$	1.9599$\times 10^{24}$(our result)	
ST– TiO$_2$	3.0344$\times 10^{25}$(our result)	

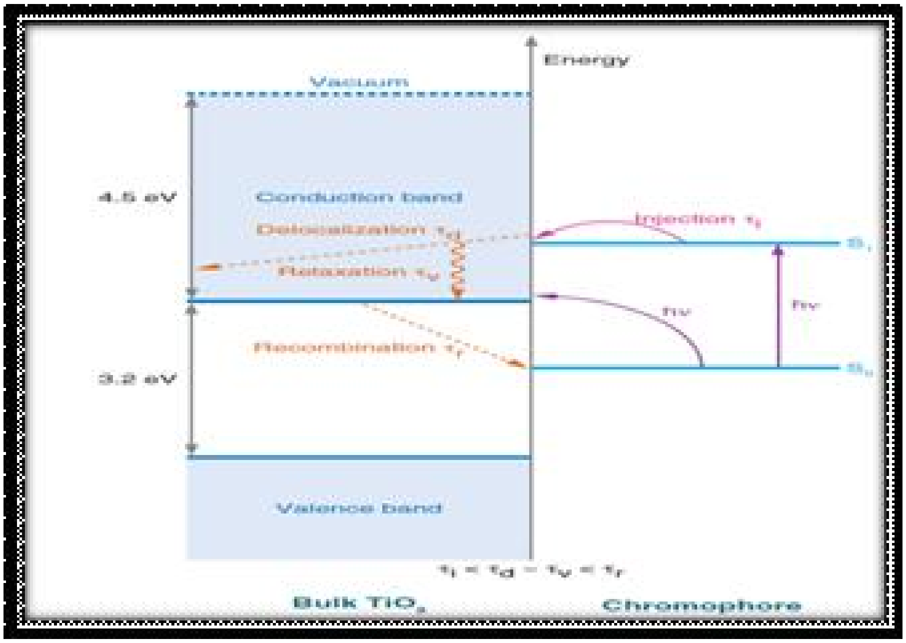

Fig. (1): The energy level Jobloniske diagram [4].

حساب معدل الانتقال الالكتروني في نظام TiO_2 صبغة السافرانين

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الخلاصة

الحسابات النظرية لمعدل الانتقال الالكتروني في نظام صبغة– شبة الموصل لمذيبات مختلفة،طبقت على نظام يحتوي على صبغة السافرانياين(ST) و شبة موصل TiO_2 ولمذيبات مختلفة مثل: الماء ،و 1–بروبانول،و الفورماميد،و اسيتونترايل ،والايثانول.

كتب برنامج ماتلاب لحساب معاملات مختلفة، مثل: طاقة اعادة الانتظام ،و الطاقة الحرة المؤثرة، والطاقة الحرة الفعالة، ومصفوفةالعوامل المرتبطة، و معدل الانتقال الالكتروني.

النتائج لمعدل الانتقال الالكتروني المحسوبة نظريا كانت ذا تطابق جيد مع نتائج حسابات البحوث العملية والنظرية.

الكلمات المفتاحية: الانتقال الالكتروني ، صبغة–شبة موصل ، نظرية الميكانيك الكمي