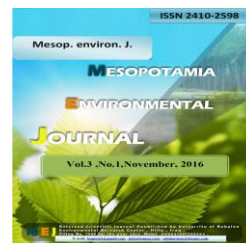




Mesopo. Environ. j., Special Issue C :24-33, 2017
ISSN 2410-2598
proceeding of 1st National conference of science and Art
University of Babylon

Mesopotemia Environmental journal
journal homepage:www.bumej.com



Theoretical Study of Electronic Transfer rate constant At Solar Cell

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To cite this article:

Al-agealy. H.J, Hassooni.M.A, Ashweik.A.M, Alshafaay.B, Mjeed. R.H. Abbas, Sadoon. A.K. Theoretical Study of Electronic Transfer rate constant At Solar Cell. *Mesop. environ. j.*, 2017, Spical Issue A.;24-33.

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Abstract

Aim of this research is theoretical investigation of the electronic transfer through the dye-semiconductor contacts solar cell devices according to the calculation the electronic transfer rate constant. Postulate of quantum mechanics is using to estimation the reorientation energy, effective free energy and rate constant at coumarin–TiO₂ and coumarin–ZnO systems. Theoretical results using to discussion the benefit of using the solar cell on the environmental depending on the calculation the electronic transfer rate cross system and that's indicate the electric properties of solar cell and efficiency to using at cleaning electric power sources. Electronic transfer rate constant is calculated depending on the estimation of the reorientation energy ,effective free energy , unit cell volume , penetration coefficient ,square overlapping coefficient, and temperature using a MATLAB designed program . In both coumarin–TiO₂ and coumarin–ZnO systems, the electronic transfer rate are increases with increases the reorientation energy and increases with effective free energy predictions.

Key world : Electronic Transfer, rate constant , Solar Cell.

Introduction

Increase of world's population that combine due to the energy growth for capita of consumption was expecting to bring an explosive rise in energy consumption. We must be saving the energy to solving these

problems.Improvement the efficiency of equipment to transform the energies and development the using of new solar energy sources .It was attractive to dealing of attention as a results for cleaning energies sources and would not be depleted. Sun's energies is one of available devices to utilized the more prominent ion first was the solar cells. The photovoltaic effect was using at semiconductor to conversion light solar energy to energy of electric [1]. However , the sensitizes electric solar cells was inventing in 1991 due to Gratzel , it was providing economically and technically credible alternatively concept to present photovoltaic cell [2].In fact, the charge separation in semiconductor p-n junction at solar cells is taken care by the junction building in electrical field .On the other hand ,charge separation in dye sensitizes solar cell was taken by kinetic competition in photosynthesis [3]. In contrast, the dye sensitized solar cell had been studied extensively to silicon-based solar cells alternatively, low production cost , flexibility, wide range of application and transparency. However of these advantages, the low efficiency of dye sensitized solar cell compared to that of silicon-based cells has limited their commercial implementation [4-5]. Despite the dye sensitized solar cell isn't limited by the harvesting light ability of the semiconductor, in fact, most are optically transparent. The sensitization of these semiconductors to visible light involves interfacial electronic transfer following selective excitation of a surface-bound molecular chromospheres [6]. Suchthe photo induced of charge-separation processing is the key step for conversion energy at solar cell. Commonly chromospheres studied would be refere to sensitizer dyes, including organic molecules and transition metal coordination compounds [7]. At recently the embodiment of the dye solar cell concept is the heterojunction sensitized cell usually using with an inorganic wide band gap nanocrystalline semiconductor of n-type polarity as electronic acceptor.The charge neutrality on the molecular dye being restored as hole delivered by the complementary semiconductor, inorganic [8-9] or organic [10] and of p-type polarity. Electronictranstion processes in the dye sensitized solar cells is a major importance for the overall performance. The focus of this paper is electronic transfer in dye sensitized solar cellssystem; this will be electronic transfer rate constant in dye /semiconductor system which is evaluated.

On the quantum theory , the electronic transfer rate constant of the donor - acceptor system state could be written as [11].

$$k_{D,A} = \frac{2\pi}{\hbar} \sum |T_{D,A}^{ET}|^2 FC_{D,A}^{ET} \dots\dots\dots(1)$$

Where \hbar is the Dirac constant, $FC_{D,A}^{ET}$ is the Franck–Condon of the density of state ,and $T_{D,A}^{ET}$ is the overlapping integrals between the donor and acceptor states . The Franck–Condon density of state $FC_{D,A}^{ET}$ in is quite estimated relative to effective energy ϵ , transfer energies Δ_{TE} and temperature T and takes the form[12].

$$FC_{D,A}^{ET} = \left(\frac{1}{4\pi\Delta_{TE} k_B T}\right)^{1/2} \exp\left[-\frac{(\epsilon+\Delta_{TE})^2}{4\Delta_{TE} k_B T}\right] \dots\dots\dots(2)$$

Where k_B is the Boltzmann constant.The Δ_{TE} is the transfer energy and means that the Δ intation and polarization of molecules around solvent in system . It indicate the reorient energy to the equilibrium of the product system and given by [13].

$$\Delta_{TE} (eV) = \frac{q^2}{8\pi\epsilon_0} \left[\frac{1}{R} \left(\frac{1}{n^2} - \frac{1}{\epsilon_{so}} \right) - \frac{1}{2d} \left(\frac{n_{sc}^2 - n^2}{n_{sc}^2 + n^2} \frac{1}{n^2} - \frac{\epsilon_{sc}^2 - \epsilon_{so}^2}{\epsilon_{sc}^2 + \epsilon_{so}^2} \frac{1}{\epsilon_{sc}^2} \right) \right] \dots\dots\dots(3)$$

Where ϵ_s is the permittivity, ϵ is the dielectric constant, n is the optical refractive index of the solvent, n_{sc} and ϵ_{sc} are the optical and static dielectric constant of the semiconductor, R is the radii of the molecular dye, and d is the distance between the molecule and the semiconductor, and q is the charge of electrons. The radii of the dye molecule can be estimated using [14].

$$R = \left(\frac{3}{4\pi N\rho} M\right)^{\frac{1}{3}} \dots\dots\dots (4)$$

Where the molecular weight M , ρ is the density and N is the number of Avogadro,.
 Inserting Eq.(2) in Eq.(1) and given by.

$$\phi_{D,A} = \frac{2\pi}{\hbar} \sum |T_{Dye/Sem}|^2 \left(\frac{1}{4\pi\Delta_{TE} k_B T}\right)^{1/2} \exp\left[-\frac{(\epsilon+\Delta_{TE})^2}{4\Delta_{TE} k_B T}\right] \dots\dots\dots(5)$$

Due to the unit cell volume of semiconductor and with penetration of electronic transfer at solar cell we can write the rate [15].

$$\phi_{D,A} = \frac{2\pi V}{\hbar \beta_S} \sum |T_{Dye/Sem}|^2 \left(\frac{1}{4\pi\Delta_{TE} k_B T}\right)^{1/2} \exp\left[-\frac{(\epsilon+\Delta_{TE})^2}{4\Delta_{TE} k_B T}\right] \dots\dots\dots (6)$$

Where the exponential function can be expanding to .

$$\exp\left[-\frac{(\epsilon+\Delta_{TE})^2}{4\Delta_{TE} k_B T}\right] = \exp\left[-\frac{\Delta_{TE}}{4k_B T}\right] \exp\left[-\left(\frac{\epsilon}{\Delta_{TE}}+1\right)^2\right] \approx \exp\left[-\frac{\Delta_{TE}}{4k_B T}\right] \left[1 - \left(\frac{\epsilon}{\Delta_{TE}} + 1\right)^2\right] \dots\dots\dots(7)$$

Substituting Eq.(7) in Eq.(5) to results.

$$\phi_{D,A} = \frac{2\pi V}{\hbar \beta_S} \sum |T_{Dye/Sem}|^2 \left(\frac{1}{4\pi\Delta_{TE} k_B T}\right)^{1/2} \exp\left[-\frac{\Delta_{TE}}{4k_B T}\right] \left[1 - \left(\frac{\epsilon}{\Delta_{TE}} + 1\right)^2\right] \dots\dots (8)$$

Where [11]

$$\epsilon = h\nu - \Delta_{TE} = h\frac{c}{\lambda} - \Delta_{TE} \dots\dots\dots(9)$$

where $h = 6.6 \times 10^{-34} \text{ J}\cdot\text{sec}$ is Planck constant, c is the light velocity ($3 \times 10^8 \text{ m/sec}$), and ν is the frequency

and equal to $\nu = \frac{c}{\lambda}$, λ is wave length for absorption spectra .

The coupling by coefficient matrix element is estimated by using [16].

$$T_{Dye/Sem} = T_{DA} \sqrt{\frac{I_{sc}}{d_{sc}^{2/3} \left(\frac{\epsilon}{n}\right)^{1/3}}} \dots\dots\dots (10)$$

Where I_{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 electronic parameter.

Results

Electronic transfer at solar cell have been studied A theoretically depending on calculation the electronic transfer rate for coumarin-TiO2 and coumarin-ZnO sensitized dye solar cell systems . Reorientation energy, effective free energy and overlapping coupling constant are active coefficients controlling on the electronic transfer in sensitized dye solar cell.

The electronic transfer as fulfillment to evaluation the reorientation energy for coumarin-TiO₂, coumarin-ZnO systems by using Eq.(3) and the physical properties for semiconductor and solvent in table (1) and (2) that are using in the present evaluation .

Table(1): The solvent properties .

| Solvent | Chemical Formula | Static dielectric constant ϵ_{so} [17] | Refractive index n [17] |
|--------------|---------------------------------|---|---------------------------|
| Water | H ₂ O | 80 | 1.333 |
| 1-propanol | C ₃ H ₈ O | 20.33 | 1.3856 |
| Formamide | HCONH ₂ | 111 | 1.4475 |
| Acetonitrile | C ₂ H ₃ N | 37.5 | 1.3441 |
| Ethanol | C ₂ H ₆ O | 24.5 | 1.3614 |

Table (2):Common properties of semiconductor.

| Semiconductor | Dielectric constant ϵ_{sc} | Refractive index n_{sc} | Energy gab (eV) | Lattice constant (nm) | Crystal structure |
|------------------|-------------------------------------|---------------------------|--------------------|-----------------------------------|-----------------------|
| TiO ₂ | 100[18] | 2.609[19] | 3.02[20] | $a = 4.5936$ $c = 2.9587$ [19] | Tetragonalrutile [19] |
| ZnO | 8.5 [21] | 2.0033[21] | $\gamma. \xi$ [21] | $a=0.3249, c=0.5206$ [21] | Wurtzite [21] |

To estimation the reorientation energies for coumarin-TiO₂, coumarin-ZnO systems, one must initially evaluate the values of the radii of coumarin dye from Eq.(4). Inserting of molecular weights $M_{co}=334.35$ [22], and densities $\rho_{co}= 1.326$ g/cm³ [22], the values of the radii is $R_{com} = 4.64227A^{\circ}$. Inserting the value of dielectric constant ϵ_{so} and refractive index n for variety solvent, and the dielectric constant ϵ_{sc} and refractive index n_{sc} for semiconductor in equation (2), with value of radii of dye and the distance between the molecule dye and semiconductor $d = R_{com} + 1A^{\circ}$, the results have been summarized in table (3) for coumarin-TiO₂, coumarin-ZnO systems system.

Table (3): The reorientation energies value for donor coumarin dye and acceptor semiconductor TiO₂ and ZnO

| Solvent | Chemical Formula | ϵ_{so} [17] | n [17] | Δ_{TE} (eV) for TiO ₂ | Δ_{TE} (eV) for ZnO |
|--------------|---------------------------------|----------------------|----------|---|----------------------------|
| Water | H ₂ O | 80 | 1.333 | 0.65458 | 0.7139 |
| 1-propanol | C ₃ H ₈ O | 20.33 | 1.3856 | 0.5579 | 0.6125 |
| Formamide | HCONH ₂ | 111 | 1.4475 | 0.5757 | 0.6299 |
| Acetonitrile | C ₂ H ₃ N | 37.5 | 1.3441 | 0.6238 | 0.6821 |
| Ethanol | C ₂ H ₆ O | 24.5 | 1.3614 | 0.5888 | 0.6452 |

On the other hand , the next coefficient for the electronic transfer rate is effective driving energy ϵ (eV) .It is supplied the solar cells by power according on the absorption of light. The effective driving energy ϵ (eV) is energy that's taking the electrons to cross interface from the molecule of dye state to the semiconductor state. It can be estimation by using Eq.(10) , where the wave length λ for coumarin is taken (400–800) nm [23] and the reorientation energy taken account from table (3). The results of ϵ (eV) for coumarin–TiO₂, and coumarin–ZnO system are listed in Tables (4), and (5) respectively.

Table (4): Effective free energy ϵ (eV) of the electronic transfer in coumarin–TiO₂ system for variety in solar cell.

| SOLVENT | Effective free energy ϵ (eV) | | | | |
|--------------|---------------------------------------|----------------------------|----------------------------|----------------------------|----------------------------|
| | $\lambda = 400 \text{ nm}$ | $\lambda = 500 \text{ nm}$ | $\lambda = 600 \text{ nm}$ | $\lambda = 700 \text{ nm}$ | $\lambda = 800 \text{ nm}$ |
| water | -2.4474 | -1.8270 | -1.4134 | -1.1180 | -0.8964 |
| 1-propanol | -2.5440 | -1.9236 | -1.5100 | -1.2146 | -0.9930 |
| Formamide | -2.5263 | -1.9059 | -1.4922 | -1.1968 | -0.9752 |
| Acetonitrile | -2.4781 | -1.8577 | -1.4441 | -1.1487 | -0.9271 |
| Ethanol | -2.5132 | -1.8927 | -1.4791 | -1.1837 | -0.9621 |

Table (5): Effective free energy ϵ (eV) of the electronic transfer in coumarin–ZnO system for variety in solar cell.

| SOLVENT | Effective free energy ϵ (eV) | | | | |
|--------------|---------------------------------------|----------------------------|----------------------------|----------------------------|----------------------------|
| | $\lambda = 400 \text{ nm}$ | $\lambda = 500 \text{ nm}$ | $\lambda = 600 \text{ nm}$ | $\lambda = 700 \text{ nm}$ | $\lambda = 800 \text{ nm}$ |
| water | -2.3880 | -1.7676 | -1.3540 | -1.0586 | -0.8370 |
| 1-propanol | -2.4895 | -1.8691 | -1.4554 | -1.1600 | -0.9384 |
| formamide | -2.4721 | -1.8517 | -1.4380 | -1.1426 | -0.9210 |
| Acetonitrile | -2.4199 | -1.7995 | -1.3859 | -1.0904 | -0.8689 |
| Ethanol | -2.4568 | -1.8363 | -1.422 | -1.1273 | -0.9057 |

However ,the electronic transfer rate constant is function of the unit cell volume of semiconductor that was shown in Eq.(10). The lattice constant for TiO₂ are a=b= 4.5936, c =2.9587[19] and a=b=3.2469 Å and c=5.2069 Å [21] for ZnO semiconductor . The TiO₂ have volume $V_{TiO_2} = 6.242 \times 10^{-23} \text{ cm}^3$ and the ZnO have volume $V_{ZnO} = 4.753 \times 10^{-23} \text{ cm}^3$.

The electronic transfer rate constant could be calculation using Eq.(8) for coumarin–TiO₂ and coumarin–ZnO for variety solvents by substituting the reorientation energy $\Delta_{TE} \text{ (eV)}$, effective free energy ϵ (ev), unit cell , volume $V(\text{m}^3)$, penetration coefficient $\beta(\text{m}^{-1})$.A MATLAB software programming have been used to calculation the electronic transfer rate constant for TiO₂-coumarin and ZnO- coumarin using Eq.(8), the results are tabulated in tables (6) and (7) for TiO₂-coumarin and ZnO- coumarin respectively.

Table (6): Electronic transfer rate constant $\rho_{D,A} \left(\frac{\text{cm}^4}{\text{sec}} \right)$ for coumarin–TiO₂ solar cell system. with variety solvents at coupling coefficient $V_{DA} = 4.032421511 \times 10^{-4} \text{ eV}$

| Solvent | Electronic transfer rate constant $\rho_{D,A} \left(\frac{\text{cm}^4}{\text{sec}} \right)$ | | | | |
|----------------------------|--|--------------------------|--------------------------|--------------------------|--------------------------|
| | Water | 1-propanol | Formamide | Acetonitrile | Ethanol |
| $\lambda = 400 \text{ nm}$ | 1.0063×10^{-42} | 4.6034×10^{-52} | 4.5514×10^{-50} | 2.5404×10^{-45} | 1.0980×10^{-48} |
| $\lambda = 500 \text{ nm}$ | 1.6178×10^{-30} | 7.0485×10^{-36} | 1.0266×10^{-34} | 5.5211×10^{-32} | 6.4940×10^{-34} |
| $\lambda = 600 \text{ nm}$ | 3.2278×10^{-24} | 2.0388×10^{-26} | 1.0492×10^{-27} | 4.5322×10^{-26} | 3.2075×10^{-27} |
| $\lambda = 700 \text{ nm}$ | 8.0314×10^{-23} | 1.0197×10^{-24} | 2.8025×10^{-42} | 2.6461×10^{-23} | 5.5207×10^{-22} |
| $\lambda = 800 \text{ nm}$ | 8.7428×10^{-22} | 7.7825×10^{-23} | 1.4237×10^{-22} | 5.0106×10^{-22} | 2.1120×10^{-22} |

Table (7) Electronic transfer rate constant $\phi_{D,A}(\frac{cm^4}{sec})$ for coumarin–ZnO solar cell system. with variety solvents at coupling coefficient $V_{DA} = 4.032421511 * 10^{-4} eV$

| Solvent | Water $k_{ET}(cm^4/sec)$ | 1-propanol $k_{ET}(cm^4/sec)$ | Formamide $k_{ET}(cm^4/sec)$ | Acetonitrile $k_{ET}(cm^4/sec)$ | Ethanol $k_{ET}(cm^4/sec)$ |
|-------------------|-----------------------------|----------------------------------|---------------------------------|------------------------------------|-------------------------------|
| $\lambda = 400nm$ | 1.3935×10^{-40} | 1.7691×10^{-48} | 6.6661×10^{-46} | 9.4217×10^{-42} | 1.3376×10^{-45} |
| $\lambda = 500nm$ | 2.7454×10^{-29} | 1.0744×10^{-33} | 8.4896×10^{-33} | 1.7888×10^{-30} | 4.6224×10^{-32} |
| $\lambda = 600nm$ | 5.0131×10^{-24} | 1.5413×10^{-27} | 5.2130×10^{-26} | 1.1183×10^{-25} | 1.3975×10^{-26} |
| $\lambda = 700nm$ | 2.9500×10^{-22} | 1.2600×10^{-24} | 2.5548×10^{-23} | 1.3821×10^{-23} | 4.4677×10^{-23} |
| $\lambda = 800nm$ | 1.2597×10^{-22} | 2.9684×10^{-22} | 4.3181×10^{-22} | 9.5544×10^{-22} | 5.7226×10^{-22} |

Discussion

The electronic transport kinetic in dye sensitized solar cell have been investigation in term of a quantum mechanical to transition through the interface region between dye and semiconductor contact. At interface , the tail of the wave functions for dye and semiconductor overlapping to facility transition of electronic at interface. According to postulate of electronic transition theory, the dye and semiconductor states are brought into resonance by fluctuations of polar medium surrounding dye and semiconductor system. This resonance is the transition state of electronic transition reaction.

Electronic transfer rate constant $\phi_{D,A}(\frac{cm^4}{sec})$ at the interface of dye-semiconductor solar sell system in Eq.() indicate the electric properties at solar cell . The electrons has been crossing over potential barrier at the interface when the two material should be alignment energy levels as result to different material structures state and different electronic density at dye surfaces and semiconductor conduction band. From the result of electronic transfer in both systems with more polar solvents like water and Acetonitrile , the reorientation energy are large for more polar solvents and small values for less polar solvents, this indicates that the reorientation energy is dependent on the polarity. Tables (3) show that the reorientation energy is lower in the less polar solvent for the coumarin–semiconductor. Consequently electronic transfer occurs most probable in polar solvents like Water, Acetonitrile. Formamide, one of the most polar solvents $\epsilon_{so} = 111$ give small reorientation energy for both of the systems as compared with other solvents that have less than dielectric constant, this indicates that Formamide have large refractive index $n = 1.4475$ as compared with other solvents. This is the reason for small reorientation energy and low value for rate constant for electronic transfer for dye –semiconductor system that is shown in tables (6) to (7). The values of the solvent reorientation energy that are calculated theoretically were fitting with the experimental

value of $\lambda = 0.7 \text{ eV}$ and 0.8 eV [12], and $\lambda = 0.5 \text{ eV}$ [24]. The transfer overlapping coefficient $T_{Dye/Sem}$, hence controls the dynamics of transition between the donor and acceptor or dye–semiconductor system and therefore of this overlapping coefficient enters into the expression for the rate of non-adiabatic electronic transfer reactions. On the other hand, the electronic transfer rate constant that is calculated showed large values for dye – semiconductor system with most polar solvent and high value for coumarin-ZnO is more reactive compare with coumarin-TiO₂ dye and ET occurs activity with polar solvents.

Tables (4) to (5) show the results of the effective free energies are negative. This indicates that effective free energies is a part of the work which can be broken to reorient of the donor–acceptor system. From tables (4) to (5) and equation (1-9), we can show the driving force depending on the reorientation energies and absorption energy. From Tables (6) to (7), one can show that the electronic transfer rate constant increases with the decrease of the effective free energy and vice versa. When a semiconductor is brought into contact with a dye, electron will flow through the interfaces until equilibrium is reached. The transfer of electron depends on the effective free energy that energy refers to the summation of redox energy and columbic energy and the solvent energy. Upon this energy, the electron will flow from semiconductor to dye until the redox energy equals Fermi energy. Also the electronic transfer are effected on the strength of the overlapping coupling at dye–semiconductor system and depending on the polarity function ,

In summary, the electronic transfer rate constant at coumarin-semiconductor depending on the reorientation energy and effective energy.

Conclusion

In summary, it can be concluded that the solar cell system has good conversion of solar energy into electricity without any effect on the environmental. The solar cell system is one important tool of energy technology devices to voiding any environmental defect. The electronic transfer reactions is strongly depending on the solvent polarity. For more polar solvents, the reorientation energies are large and take small values for less polar solvents. The electronic transfer rate constant is large in both of the systems (dye –semiconductor) with solvent more polarity than these less polarity. Electronic transfer rate constant is large in coumarin–ZnO solar cell and indicates the dye is more reactive towards ZnO than TiO₂. The difference between the calculated results for dye –ZnO and dye –TiO₂ may be due to density of semiconductor states that are proportional with the volume of semiconductor.

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