دراسة نظرية لتأثير نوع المذيب في طاقة اعادة الألتحام في نظام (صبغة- شبه موصل) "

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الخلاصة

الحسابات النظرية لطاقة أعادة الالتحام قد أجريت لنظام شبه موصل (ZnO،TiO_2) الصبغات العضوية (السافرانين T ،الكومارين) ولمذيبات مختلفة مثل الماء، 1—بروبانول، فورمامايد ، استونترايل ،والأيثانول.وتبين أن قيم طاقة إعادة الالتحام لنظام (صبغة_شبه موصل) كبيرة للمذيبات ذات القطبية العالية (للماء $\lambda = 0.741$ ، اسيتونترايل $\lambda = 0.708$ ،ايثانول $\lambda = 0.669$) وقليلة للمذيبات ذات القطبية الواطئة (1-بروبانول $\lambda = 0.635$).طاقة اعادة الالتحام لنظام (صبغة سافرانين T_شبة الموصل) كانت قيمتها اكبر ($635-0.741$) منها لنظام (صبغة الكومارين_شبة الموصل) ($0.612-0.731$) والمذيبات أنفسها وهذا يشير الى أن صبغة السافرانينT اكثر فعالية لتفاعل الانتقال الالكتروني شبه الموصل .

A Theoretical Study of the Effect of The Solvent Type on The Reorganization Energies of Dye - Semiconductor System Interface

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Abstract

A theoretical calculation of the reorganization energies is demonstrated for semiconductor (TiO_2, ZnO) and organic dye (safranine T, and coumarin) with a variety solvent such that (water, 1-propanol, Formamide, Acetonitrile and Ethanol).

The reorganization energy values for dye –semiconductor interface system are large in high polar solvent (water $\lambda = 0.741$, Acetonitrile $\lambda = 0.708$, Ethanol $\lambda = 0.669$) and small in low polar solvent(1-propanol $\lambda = 0.635$. The reorganization energy in safranine T –semiconductor system is larger ($0.741 - 635$)than in coumarin –semiconductor for with the same solvents ($0.731 - 0.612$), this indicates that safranine T dye one more electron transfer reactive towards semiconductor.

Introduction

Electron transfer (ET) between molecular adsorbaies and semiconductor has been a subject of intense research interests for many years [1]. The understanding of this fundamental process is essential for the application of semiconductor in photography, solar energy comersion, wase degradation, and nano_scale devices [2]. One of these examples is the electron transfer between dyes and semiconductor plays a vital role in silver halide photography, electrophotography, and more recently in solar energy cell [3].

Since the seminal work predicting solvent dynamical control of electron transfer reactions in the early 1980s, a great deal of theoretical effort has gone into clarifying the salvation dynamics electron transfer connection [4]. Consequently, there is a great interest in understanding how the physical properties control the direction and rate of electron transfer. The key factor controlling the rate of electron transfer, is the reorganization energy, which describes the energy necessary to distort the nuclear configuration from its equilibrium donor state to the acceptor state without transfer of an electron. Many theories were used to calculate the reorganization energies one of these is a continuum model that is used in our research to calculate the reorganization energies in dye _semiconductor system for different solvents [5]. In this paper we can use the continuum solvent model to calculate the reorganization energy for safranine T dye_TiO_2, ZnO and coumarin dye _ TiO_2, ZnO.

Theory

The standard Marcus diagram describes the energy surface of the donor (reactant) and acceptor (product) states as a function of the nuclear configuration coordinate [5]. According to the Marcus cross relation the reorganization energy, λ, is defined as the energy necessary to distort the nuclear configuration from its equilibrium donor state to the acceptor [6].

In figure (1) the ΔG^* is the activation energy, ΔG° is the free energy, λ is the reorganization energy .This reorganization energy can be broken down further into inner and outer sphere components [7,8].

$$\lambda = \lambda_{in} + \lambda_{out} \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

The inner sphere reorganization component (λ_{in}) is the intra molecular or inner shell is the energy required to alter bond distances and bond angles with the change in oxidation state. The sphere reorganization λ_{out} is the energy required for reorientation of the solvent around the changed complexes [9].

The solvent independent term λ_{in} arises from structural differences between the equilibrium configurations of the reactant and product states; this is the sum of all the molecular vibrational and rotational movements [8].In the harmonic approximation, it can written as [10].

$$\lambda_{in} = \frac{1}{2} \sum k_i (r_i^{eq(R)} - r_i^{eq(P)})^2 \quad \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

Where k_i is the reduced force constant for the i –th vibration $r_i^{eq(R)}$ and $r_i^{eq(p)}$ are the equilibrium bond lengths in the reactant and product states, respectively, and the sum is taken over all active intra molecular. Vibration which are part to the reaction coordinate. The solvent dependent outer term λ_{out} is called solvent reorganization energy and arises from differences between the orientation and polarization of solvent molecules around $D^+ A^-$ and D A [11]. It represents the energy necessary to reorient the solvent molecules around the new equilibrium geometry of the product, but neglecting the additional effects due to electron transfer [11]. By treating the solvent as a dielectric continuum the following expression can be derived for λ_{out} [12].

$$\lambda_{out} = \frac{1}{2\pi\varepsilon_{\circ}}\frac{q^{2}}{4}\left[\frac{1}{D}\left(\frac{1}{n^{2}}-\frac{1}{\varepsilon}\right)-\frac{1}{2R}\left(\frac{n_{sc}^{2}-n^{2}}{n_{sc}^{2}+n^{2}}\frac{1}{n^{2}}-\frac{\varepsilon_{sc}^{2}-\varepsilon^{2}}{\varepsilon_{sc}^{2}+\varepsilon^{2}}\frac{1}{\varepsilon^{2}}\right)\right] \quad ..(3)$$

Where $\varepsilon_{\circ}$ 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 [13].

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

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

Results

To calculate the reorganization energies for the systems safranine T- TiO_2, safranine T-ZnO, coumarin-TiO_2, coumarin-ZnO theoretically using the equation (3), one must initially evaluate the values of the radii for both dyes safranine T and coumarin from equation (4),respectively. Inserting of molecular weight M_{sa}=350.85, M_{co}=334.35, and density ρ_{sa}=1.5487 mg/m^3 , ρ_{co} = 1.326 mg/m^3 [14,15]. For safranine T and coumarin respectively, the values of radii are D_{sa}=4.47820 A°, and D_{co}=4.64227 A°.

Inserting the value of dielectric constant ε and refractive index ***n*** for variety solvent, and the dielectric constant ε_{sc} and refractive index n_{sc} for semiconductor in equation (3), with value of radius of dye and the distance between the molecule dye and semiconductor ***R*** ,the results have been summarized in Tables(1)and (2).

Discussion

For both systems (safranine T– semiconductor) and (coumarin– semiconductor), the solvent reorganization energy values, λ are calculated according to the dielectric continuum models for electron transfer reactions. The value of reorganization energy for (safranine T-ZnO) system is larger than that of the (safranine T-TiO_2) system with the same solvent. Also the value of reorganization energy for coumarin –ZnO system is larger than that of the coumarin –TiO_2 system with the same solvent. Since safranineT-semiconductor and coumarin- semiconductor system with water solvent possesses is a more reorganization energy than the other solvent. Notably, from Table (1) and Table (2) the dynamic of the reorganization energy is solvent dependent, and the reorganization energy is lower in the less polar solvent compared with higher than polar solvent for the both systems (safranine T-semiconductor) and (coumarin-semiconductor) alternatively. Formamide, one of the polar solvent (ε =111)gives small reorganization energies for both system compare with other solvents that have less ε , this indicates that formamide have large refractive index n =1.4475 in comparison with other solvents .The reorganization energies in safranine T –semiconductor is larger than in the coumarin- semiconductor system with the same solvent, this indicate that the reorganization energy is depending on the radius of the dye for safranine T (D_{sa} =4.47820 A° , D_{co} =4.64227 A°).

The results of the reorganization energy in Table (1) and Table (2) lead to suggest that electron transfer is most probable in safranineT -semiconductor system than coumarin-semiconductor with the same solvents. Notably, the electron transfer in safranineT –ZnO and coumarin –ZnO system are stronger than in safranineT –TiO_2 and coumarin –TiO_2 system with the same solvent

Conclusions

In summary, it can be concluded from the present results that the reaction of electron transfer strongly depends on the solvents polarity. For high polar solvents, the values of the reorganization energies are large and small for low polar solvents, this indicates that, the reorganization energies depend on the polarity of the solvent.

Consequently, large values of the reorganization energy in coumarin and safranineT dyes with ZnO semiconductor indicate that ZnO is more reactive towards safranineT and coumarin than TiO_2 semiconductor.

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Table (1): The reorganization energies value for donor safranineT dye and acceptor semiconductor TiO_2 and ZnO

Solvent	**Chemical Formula**	**$\mathcal{E}$ [16]**	***n* [16]**	**λ(eV) for TiO_2**	**λ(eV) for ZnO**
Water	H_2O	80	1.333	0.6798942561	0.7410583182
1-propanol	C_3H_8O	20.33	1.3856	0.5795911754	0.6357856215
Formamide	$HCONH_2$	111	1.4475	0.5978483206	0.65367811001
Acetonitrile	C_2H_3N	37.5	1.3441	0.6480338344	0.7080101686
Ethanol	C_2H_6O	24.5	1.3614	0.6116580688	o.6697502622

Table (2): The reorganization energies value for donor coumarin dye and acceptor semiconductor TiO_2 and ZnO

Solvent	Chemical Formula	ε [16]	n [16]	λ(eV) for TiO_2	λ(eV) for ZnO
Water	H_2O	80	1.333	o.6545818996	0.7139673890
1-propanol	C_3H_8O	20.33	1.3856	0.5579871463	0.6125475297
Formamide	$HCONH_2$	111	1.4475	0.5757477988	0.6299473232
Acetonitrile	C_2H_3N	37.5	1.3441	0.6238838374	0.6821161364
Ethanol	C_2H_6O	24.5	1.3614	0.5888491116	0.6452520583

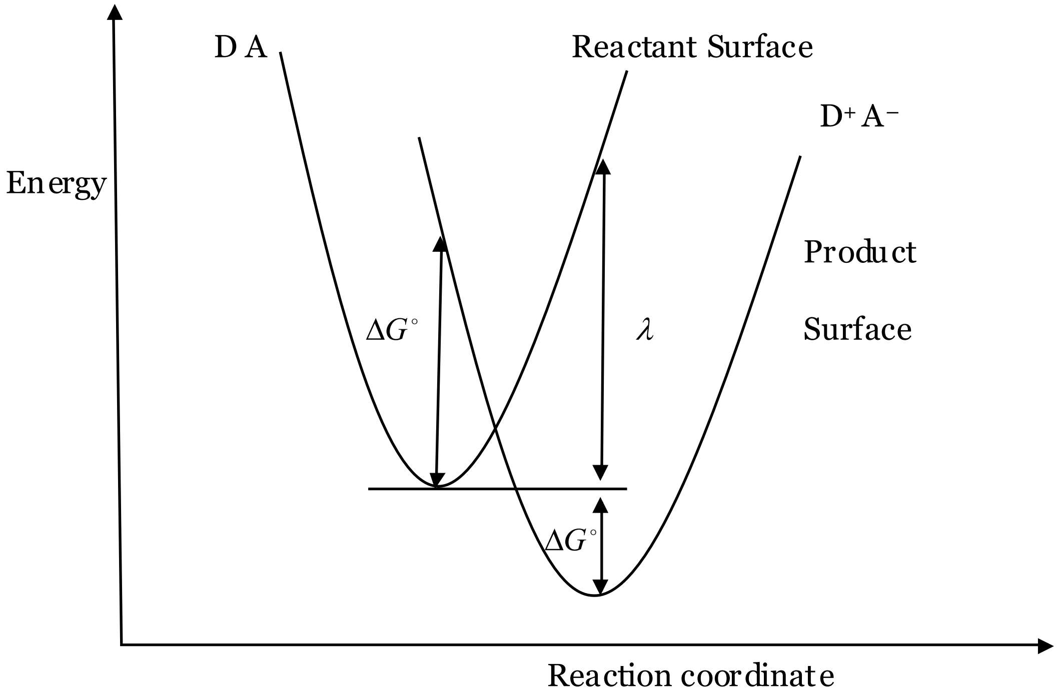

Fig. (1):Energy surface and kinetic parameters for an electron transfer reaction, ΔG° is the free energy , λ is the reorganization energy [7]