

Effects of Driving Force Energy ΔV° (eV) on the Rates of Electron-Transfer Reactions at Metal/Liquid Interface

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ABSTRACT

Electron transfer (ET) in metal/liquid interface exhibits dependence on the driving free-energy ΔV° . It has been studied depending on the quantum theory. The driving force energies ΔV° for the electron transfer reaction are calculated as a function of the reorganization energy $E_{\text{met}}^{\text{liq}}$, and absorption energy E_{abs} when a light is incident on the donor-acceptor system. The results show that the driving force energy ΔV° for electrons increase with increases absorption energy and decreasing with wave length and reorganization energy $E_{\text{met}}^{\text{liq}}$. A MATLAB program has been used to calculate the reorganization energy $E_{\text{met}}^{\text{liq}}$, driving free energy ΔV° , and the rate constant of electron transfer $\mathfrak{R}_{\text{ET}}$. The present results show that the rate constant $\mathfrak{R}_{\text{ET}}$ increases with the increasing of the reorganization energy $E_{\text{met}}^{\text{liq}}$, and with the decreasing of the driving force energy ΔV° . Probability of electron transfer occurs in most polar solvent $f(\mathbf{n}, \epsilon)$ system and has low driving force energy.

Keywords: Driving Force, Electron transfer, Metal/Liquid Interface

تأثير طاقة القوة الدافعة $\Delta V^\circ (eV)$ على ثابت معدل الانتقال الالكتروني لوصلة سطح معدن /سائل

الخلاصة

أن الانتقال الالكتروني في وصلة معدن /سائل أعتمد على القوة الدافعة للكترونات وقد درس أعتماذا على أنموذج نظري . طاقة القوة الدافعة للالكترونات حسبت كدالة لطاقة اعادة الترتيب و الطاقة الممتصة عندما يسقط الضوء على نظام مانح-مستقبل. قيم طاقة القوة الدافعة للالكترونات تزداد مع زيادة الطاقة الممتصة وتناقص الطول وطاقة إعادة الترتيب. برنامج ال MATLAB استعمل لحساب طاقة القوة الدافعة للالكترونات و وطاقة اعادة الترتيب ومعدل الانتقال الالكتروني. لقد اظهرت النتائج ان معدل الانتقال الالكتروني يزداد مع زيادة طاقة اعادة الترتيب وتناقص طاقة القوة الدافعة للكترونات. أن احتمالية الانتقال الالكتروني تحدث لنظام له استقطابية عالية وطاقة قوة دافعة للالكترونات قليلة.

Introduction

Electron transfer reactions represent 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 reactions. It is one of the most important reaction in physical chemistry and biology involves an oxidation of donor state $|D\rangle$ and reduction of an acceptor state $|A\rangle$ [1].

The electron transfer reaction rate could be as fast as 1PecoSec^{-1} and as slow as 1Year^{-1} , depending on reactions environmental conditions. An electron transfer reaction may occur between an electrode and molecule or ion (heterogeneous) or between two molecule or ions (homogeneous and bimolecular) or between the two constituents of the same molecule or ion (homogenous and unimolecular) [2]. Electron transport at the

Nano scale is remarkably essential to many processes in nature and is therefore an important subject in scientific disciplines such as biology, chemistry, and physics. Electron transfer processes are also essential in electrochemistry which concerns the reactions taking place at the interface between electronic conductors and ionic conductors [3]. It should be noted that the particle that is actually transferred in redox reactions need not always be just a single electron [4]. Rudolph Marcus described electron transfer between two states, a model which was the basis for the classical theory of electron transfer. Latter, this model was extended to describe electron transfer from a single donating state to a continuum of accepting state [5]. Understanding transport across the interface between the active organic molecule and the metallic electrode has proved particular challenging, especially in the single molecule limit. Electron transfer between a

molecular and a metal surface is a ubiquitous process in many chemical disciplines, ranging from molecular electronics to surface photochemistry. Subsequent evolution of the excited electronic wave function is probed in energy, momentum, and time domains by the absorption of a photon. These experiments studies reveal the important roles of molecule/metal wave function mixing, intermolecular band formation, polarization, and localization in interfacial electron transfer [6].

The field of electron transfer has been greatly advanced by the detailed analytical theory in the past half century ago depending on the standards theory and also by introduction a new technology, such as photochemical initiation [7]. The aim of this work is the study of the effect the driving force energy on the electron transfer rate constant at Cu metal with 1,4,5,8-naphthalene tetra carboxylicdiimide molecule interface system; that is calculated theoretically depending on the reorganization energy.

Theory

The rate of the electron transfer from a discrete donor state to continuum acceptor state is the time derivative of the probability which is given by [8].

$$\mathfrak{R}_{ET} = \frac{2\pi}{\hbar} \int_{-\infty}^{\infty} |\mathcal{H}_{DA}(E)|^2 (4\pi E_{\text{met}}^{\text{liq}} k_B T)^{-\frac{1}{2}} \exp \left(\frac{-(E_{\text{met}}^{\text{liq}} + \Delta V)^2}{4E_{\text{met}}^{\text{liq}} k_B T} \right) F_{(E)} \delta(E_m - E_n) dE \dots \dots \dots 1$$

where $\hbar$ is the Planck constant divided by 2π , $|\mathcal{H}_{DA}(E)|^2$ is the coupling matrix element between the electronic state of the metal and the molecule of liquid, $E_{\text{met}}^{\text{liq}}$ is the reorganization energy, k_B is the Boltzmann constant, T is absolute temperature, and $F_{(E)}$ is the Fermi-Dirac probability distribution of the electrons in the electron metal-liquid interface and given by [9].

$$F_{(E)} = \frac{1}{1 + \exp \frac{E}{k_B T}} \dots \dots \dots (2)$$

For electron transfer in metal/liquid interface system, the rate constant of electron transfer at metal/liquid interface can be got by substituting Eq.(2) in Eq.(1), and solving the integration Eq.(1), one gets [10].

$$\mathfrak{R}_{ET} = \frac{2\pi}{\hbar} (4\pi E_{\text{met}}^{\text{liq}} k_B T)^{-\frac{1}{2}} \exp - \frac{E_{\text{met}}^{\text{liq}}}{4k_B T} |\overline{\mathcal{H}_{DA}(0)}|^2 \left[\left[1 - \frac{1}{4E_{\text{met}}^{\text{liq}} k_B T} \left(\frac{\pi k_B T}{4} \right)^2 \right) + \frac{1}{32E_{\text{met}}^{\text{liq}^2} k_B^2 T^2} \left(\frac{5(\pi k_B T)^4}{16} \right) - \frac{1}{384E_{\text{met}}^{\text{liq}^3} k_B^3 T^3} \left(\frac{61(\pi k_B T)^6}{64} \right) \dots \dots \dots + \frac{1}{n! (4E_{\text{met}}^{\text{liq}} k_B T)^n} (\propto (\pi k_B T)^{2n}) \right] \dots \dots \dots (3)$$

The reorganization energy $E_{\text{met}}^{\text{liq}}$ due to the electron transfer reaction for metal/liquid interface is given by [11].

$$E_{\text{met}}^{\text{liq}} = \frac{e^2}{8\pi\epsilon_0} f(n, \epsilon) \left(\frac{1}{R} - \frac{1}{2D} \right) \dots \dots (4)$$

where e is the electron charge, ϵ_0 is the vacuum permittivity, D is the distance between the complex and electrode, R is the radius of the molecule and $f(n, \epsilon)$ is the polarity function $f(n, \epsilon)$ that given by.

$$f(n, \epsilon) = \left(\frac{1}{n^2} - \frac{1}{\epsilon}\right) \dots \dots \dots (5)$$

Where ϵ is the static dielectric constant of the solvent, n is the refractive index of the solvent.

The radius of the molecule can be estimated from the apparent molar volume using spherical approach [12].

$$R = \left(\frac{3M}{4\pi N\rho}\right)^{\frac{1}{3}} \dots \dots \dots (6)$$

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

The driving force energy ΔV° of the electron transfer reaction is a function for the absorption energy E_{abs} and the reorganization energy E_{met}^{liq} is given by [13].

$$\begin{aligned} \Delta V^\circ &= E_{abs} - E_{met}^{liq} \\ &= hf - E_{met}^{liq} \dots \dots \dots (7) \end{aligned}$$

Where h is the Planck constant, f is the frequency, $f = \frac{c}{\lambda}$ where c is the velocity of light, and λ is the wave length.

Results

One of the most important parameter for the Studies of the electron transfer rate constant at metal/liquid interface is the driving force energy ΔV° (eV) that can be calculated theoretically using Eq. (7).

The absorption energy $E_{abs} = hf$

can be roughly taking from the wave length λ for the spectrum region (350nm-800nm) and transform energy equation $\frac{hc}{\lambda}$, where $h = 4.135667334 \times 10^{-15} \text{ eV} \cdot \text{sec}$, c is the velocity of light $3 \times 10^8 \text{ (m/sec)}$.

The reorganization energies E_{met}^{liq} (eV) for the electron transfer have been evaluated using Eq.(4-5) with the values of the static dielectric constant, and optical dielectric constant ϵ_{op} , for solvents from table (1).

The radius for donor and acceptor system are estimated using approach in Eq.(6) with the values of Avogadro's constant $N = 6.02 \times 10^{23} \frac{\text{Molecule}}{\text{mol}}$, molecular weight $M = 302.24$ [15], density ρ is 1.751 g/cm^3 [16] for 1,4,5,8-naphthalene tetracarboxylic diimide molecules and molecule weight

$M = 63.546 \text{ g} \cdot \text{mol}^{-1}$, and $\rho = 8.92 \text{ g} \cdot \text{cm}^{-3}$ for Cu metal [14] in Eq.(6). The estimation of the values of radii are $1.41343 \text{ \AA}$ and $4.089977 \text{ \AA}$ for Cu metals and of 1,4,5,8-naphthalene-tetracarboxylic diimide molecules respectively.

The driving force energies ΔV° (eV) is provided the electrons to transfer cross interface. It is related to the difference between the reorganization energy from table 1 and the absorption energy spectra (350nm-800nm), results are summarized in table 2.

The rate constant of the electron transfer at semiconductor/liquid interface was calculated using Eq.(3) with a Matlab designed program and inserting the result of the reorganization energy from table (1) , the matrix element coupling coefficient [17], driving force energy from table (2) ,and temperature is taken $T=300K$,results are shown in table (3).

Table 3 shows the results of the rate constant for electron transfer at Cu metal/ 1,4,5,8-naphthalene tetra carboxylic diimide molecule liquid interface with variety coupling coefficient $\mathcal{H}_{DA}$.

Discussion

Electron transfer interactions at metal/molecule interface system should be effected by polarity parameter for the solvent molecules. The reorganization energy E_{met}^{liq} (eV) is large for large polarity function and vice versa, this indicates that the reorganization energy E_{met}^{liq} (eV) is a function of the polarity of the solvent. The probability of electron transfer $\mathfrak{R}_{ET}(Sec^{-1})$ across the interface created between metal and molecule in solvent system depends on the reorganization energy E_{met}^{liq} (eV), driving force

energy ΔV° (eV) and the coupling coefficient $|\mathcal{H}_{DA}(E)|$ (eV). The probabilities of rate constant $\mathfrak{R}_{ET}(Sec^{-1})$ at metal/molecule system are depending on the organization energy E_{met}^{liq} (eV) of the electron transfer. It is calculated depending on continuum Marcus theory with the physical concepts such as a refractive index, and static dielectric constant for donor/ acceptor system.

Results of the driving force energy ΔV° (eV) in table 2 for electron transfer is take term accounting for the drive more electron to transfer across interface, that describe the interactions between of the donor state wave function and acceptor state wave function. Results of the driving force energy show that the drive energies ΔV° (eV) for electrons as a function of the reorganization energy and the absorption energy at region (350-800) nm. Table 2 of the driving force ΔV° (eV), show that its energies that take to bring the donor and acceptor together and is the part of the work broken to derive the electrons to transfer from donor to acceptor. The driving force energy ΔV° (eV) to drive the electron increases with increases absorption energy and decreasing in wave length and reorganization energies for system. Furthermore, the reorganization energy E_{met}^{liq} (eV) and the driving force energy ΔV° (eV) and the coupling coefficient energy are the base of electron transfer in system. Data of rate constant depending on these parameters enable to understand the idea of

the behavior of electron transfer in metal/molecule

Data of ET rate constant $\mathfrak{R}_{ET}(Sec^{-1})$ that occur in metal/molecule system with lest polarity function solvents, that's view from comparing between tables 1 and 2.

On the other hand, the rate constant $\mathfrak{R}_{ET}(Sec^{-1})$ values are large for system with lest polarity function and low values of reorganization energy, this indicates that Ethyleneolamine and Dimethylsulfoxid 1 are more reactive towards metal than others and ET occur activity with less polar solvents. Table 3 gave the theoretical results for rate constant of electron transfer and show that rates are increasing with increasing of the driving force energy. This because of when the system have low reorganization energies make the driving force energy become large and finally more electrons that transfer the interface between metal and molecules and vice versa .On the other hand, the absorption energy divided to reorientation the system to transfer and the other enable to drive the electron to transfer due to tunneling height from donor to acceptor and the rates are increasing.

Another controlling of electron transfer is the coupling coefficient $|\mathcal{H}_{DA}(E)|(eV)$ that can be assume in the range $(0.000111- 0.000186) (eV)^2$ for metal/molecule system according the experimental data [17]. At interface between metal and molecule, the wave functions for metal and molecule overlapping and electron

can be transfer due tunneling. However, if the electron tunneling occurs, the initial and final electronic states should have approximated equal energies that happen under the considering continuum of electronic states for the metal/molecule system interfaces. These electronic states are brought into resonance by fluctuations of polar medium surrounding metal and molecule system and this resonance is the transition state of electron transfer reaction.

Conclusions

In conclusion the probability of electrontransfer $\mathfrak{R}_{ET}(Sec^{-1})$ across the interface created between metal and molecule in solvent system depends on the reorganization energy $E_{met}^{liq}(eV)$, driving force energy $\Delta V^{\circ}(eV)$ and the coupling coefficient $|\mathcal{H}_{DA}(E)|(eV)$.

Driving force energy $\Delta V^{\circ}(eV)$ for electron transfer is a function of the reorganization energy and the absorption energy take term accounting for the drive more electrons to transfer across interface, and describe the interactions between of the donor state wave function and acceptor state wave function. The driving force energy $\Delta V^{\circ}(eV)$ to drive the electron increases with increases absorption energy and decreasing in wave length and reorganization energies for system.

Electron transfer rate constant $\mathfrak{R}_{ET}(Sec^{-1})$ that occur in metal/molecule system with lest polarity function and low values of reorganization energy and show that rates are increasing with increasing of the driving force energy due to tunneling

height from donor to acceptor and the rates are increasing. At interface between metal and molecule, the wave functions for metal and molecule overlapping and electron

can be transfer due tunneling and electronic states are brought into resonance by

fluctuations of polar medium surrounding metal and molecule system and this resonance is the transition state of electron transfer reaction.

Table 1. The results of the reorganization energy $E_{\text{met}}^{\text{liq}}(\text{eV})$ for electron transfer at Cu/ for 1,4,5,8- naphthalene tetra carboxylicdiimide molecule interface system.

Solvent	$f(n, \epsilon)$	Refractive index[14]	Dielectric constant[14]	Reorganization energy
Methanol	0.5377	1.3265	32.70	0.594
Acetonitrile	0.5289	1.3416	37.50	0.585
Ethylenimine	0.4467	1.4123	18.30	0.494
Fornicacid	0.5161	1.3694	58.50	0.571
Propionitnile	0.5010	1.3636	27.20	0.554
Ethyleneolamine	0.3972	1.4513	12.90	0.439
Propanol-1	0.4731	1.3837	20.33	0.523
Benzen	0.00519	1.5011	2.28	0.005
Dimethylsulfoxidl	0.4367	1.4773	46.68	0.483
Vale-onirile	0.4601	1.3991	19.71	0.509

Table 2. The results of the calculated driving free energy $\Delta V^\circ(\text{eV})$ for the electron transfer in Cu/1,4,5,8- naphthalene tetra carboxylicdiimide systems with ten solvents.

Solvent Type	$\Delta V^\circ(\text{eV})$									
	Wave length									
	350nm	400nm	450nm	500nm	550nm	600nm	650nm	700nm	750nm	800nm
Methanol	2.95034	2.50719	2.16251	1.88677	1.66117	1.47317	1.31409	1.17773	1.05956	0.95616
Acetonitrile	2.96008	2.51693	2.17226	1.89652	1.67091	1.48291	1.32383	1.18747	1.06930	0.96590
Ethylenimine	3.05103	2.60788	2.26320	1.98746	1.76186	1.57386	1.41478	1.27842	1.16025	1.05685
Fornicacid	2.97419	2.53104	2.18637	1.91063	1.68502	1.49702	1.33794	1.20159	1.08341	0.98001
Propionitnile	2.99092	2.54777	2.20310	1.92736	1.70176	1.51375	1.35467	1.21832	1.10014	0.99674
Ethyleneolamine	3.10574	2.66259	2.31792	2.04218	1.81657	1.62857	1.46949	1.33314	1.21496	1.11156
Propanol-1	3.02183	2.57868	2.23400	1.95826	1.73266	1.54466	1.38558	1.24922	1.13105	1.02765
Benzen	3.53946	3.09631	2.75163	2.47589	2.25029	2.06229	1.90321	1.76685	1.64868	1.54528
Dimethylsulfoxidl	3.06201	2.61886	2.27418	1.99844	1.77284	1.58484	1.42576	1.28940	1.17123	1.06783
Vale-onirile	3.03619	2.59304	2.24836	1.97262	1.74702	1.55902	1.39994	1.26358	1.14541	1.04201

Table 3. The results of the rate constant for electron transfer at Cu metal/ 1,4,5,8-naphthalene tetra carboxylicdiimide molecule liquid interface with variety coupling coefficient $\mathcal{H}_{DA}$.

Solvent Type	The electron transfer rate constant $\mathfrak{K}_{ET}(\text{Sec}^{-1})$			
	$\mathcal{H}_{DA}(0)$ = 0.01115 eV	$\mathcal{H}_{DA}(0)$ = 0.01177eV	$\mathcal{H}_{DA}(0)$ = 0.01239eV	$\mathcal{H}_{DA}(0)$ = 0.01363eV
Methanol	1.627E+09	1.814E+09	2.010E+09	2.432E+09
Acetonitrile	1.773E+09	1.975E+09	2.189E+09	2.649E+09
Ethylenimine	3.904E+09	4.350E+09	4.820E+09	5.833E+09
Formicacid	2.006E+09	2.235E+09	2.477E+09	2.997E+09
Propionitnile	2.321E+09	2.586E+09	2.866E+09	3.468E+09
Ethyleneolamine	6.222E+09	6.933E+09	7.683E+09	9.298E+09
Propanol-1	3.035E+09	3.382E+09	3.748E+09	4.535E+09
Benzene	-9.726E+12	-1.083E+13	-1.201E+13	-1.453E+13
Dimethylsulfoxidl	4.289E+09	4.779E+09	5.296E+09	6.409E+09
Vale-onirile	3.436E+09	3.828E+09	4.242E+09	5.134E+09

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