Barrier for Charge Transfer at Liquid/Liquid Interface

Al-Agealy Hadi J.,M., and Al-Saadi Adil.A.,M.

Department of Physics, College of Education Ibn-Al-Haitham, University of Baghdad

Abstract

The height potential barrier $\Delta G^{++}(eV)$ of charge transfer at liquid/liquid interface was described and calculated on the base of the semi classical theory. It is a function of the reorganization energy, and driving force energy respectively. Results of the reorganization energy E_0 indicate that the charge transfer is more probable in liquid/liquid system which has more polarity parameter. Charge transfer in system has large dielectric constant are stronger than system that have small dielectric constant. The driving force energy for charge transfer is the energy that takes to bring the donor and acceptor together and drive the charge increases with the increase of absorption energy and decrease in wave length. Results of height barrier $\Delta G^{++}(eV)$ across liquid/liquid interface decreases with the decrease of the driving force energy and increasing of the absorption energies. The transition is so much small as a barrier has large values but in the low values of barrier, the transfer is most probable. The large height barrier exclusion transfer across liquid/liquid system and the charge suffering much resistant to transfer.

Key Words: height potential barrier, charge transfer, liquid/liquid interface.

تأثير ارتفاع بئر الجهد على انتقال الشحنة عبر وصلة سائل/سائل

هادي جبار مجبل العكيلي و عادل علي منصور السعدي

خلاصة

وصف ارتفاع حاجز جهد لانتقال الشحنة عبر وصلة سائل/سائل وحسبت على اساس النظرية شبه الكلاسيكية. حاجز بئر الجهد هو دالة لطاقة اعادة الترتيب وطاقة القوة الدافعة للالكترونات على التتالي. تشير نتائج طاقة اعادة الترتيب E_0 الى ان انتقال الشحنة اكثر احتمالا في نظام سائل/سائل الذي يملك معامل استقطابية عالية. انتقال الشحنة في نظام يملك ثابت عزل عالي اقوى من نظام يملك ثابت عزل صغير. طاقة القوة الدافعة لانتقال الشحنة هي التي تأخذ الواهب والمستقبل سوية وسوق الالكترونات يزداد مع زيادة الطاقة الممتصة وبتناقص الطول الموجي. نتائج حاجز الجهد ΔG^{++} عبر وصلة سائل/سائل يتناقص بتناقص القوة الدافعة وبزيادة الطاقة الممتصة. الانتقال يكون قليل لحاجز عالي الارتفاع ولحاجز ذو سطح قليل الارتفاع يكون الانتقال اكثر احتمالا. ارتفاع الحاجز العالي يمنع الشحنة لعبور الوصلة سائل/سائل والالكترون يعاني ممانعة اللانتقال.

الكلمات المفتاحية: ارتفاع بئر الجهد، أنتقال الشحنة عبر وصلة سائل/سائل.

Introduction

Charge transfer (CT) from a liquid donor state to an acceptor liquid state is one of the simplest conceivably reactions as chemical bond are neither formed nor broken. Charge transfer through molecular framework of vital important to a wide range variety of processes in physical chemistry, and biological [1]. For example charge transfer in primary step in photosynthesis and various chemical reactions. The studies of charge transfer in organic molecular systems have witnessed a rapid growth in recent years [2]. The charge transfer is of highly importance in bioenergetics and is an active field of research. Much attention has been devoted to studying the charge transfer at liquid /liquid interface and molecular transport reaction processes [3]. As a result ,the donor becomes oxidized and the acceptor will be reduced .reactions which involve the transfer of an electron are called redox reactions .redox reactions play an important role in everyday life, for example, the sequence of reactions which sustain the metabolism in plants and animals consists entirely of redox reactions[4] .

The first observation of electron transfer reaction in solution goes back in the nineteenth century, when Humphrey Davy observed (1808) that passing ammonia over metallic potassium produces a fine blue color [5]. Since the late 1940 s, the field of electron transfer processes have grown enormously, both in chemistry and biology. The development of the field

Theory

The probability of charge transfer from donor liquid state to an acceptor liquid state is given by[8].

$$W_{DLAL}=\frac{2\pi}{\hbar}\,|T_{DA}|^2 \quad \rho(E_{DL}-E_{AL}-\hbar\omega) \text{ ....(1)}$$

Where $\hbar$ the plank constant divided by 2π, T_{DA} is the coupling matrix element, and $\rho(E_{DL}-E_{AL}-\hbar\omega)$ is the probability of finding the liquid-liquid system in the energy states E_{DL}, and E_{AL} are appreciable only when one or the other of the two terms is close to zero .

of the electron transfer experimentally and theoretically, as well as its relation to the study of other kinds of chemical reactions [6].

The classical transfer theory was initially generalized for the liquid |liquid coupling interface by Samec. Giraultand Schifrin considered the electron transfer reaction as asides of steps, where the formation of a precursor complex of the reactants is followed by reorganization of the precursor, charge transfer and dissociation of the products [7].

The present study focus on the description and studying the charge transfer potential barrier height at liquid/liquid system; this will be calculated theoretically according to values of reorganization energy and the driving force energy.

Assuming that $E_{DL} > E_{AL}$, then $\rho(E_{DL}-E_{AL}-\hbar\omega)$ is positive and the probability of transition may be enable to write [9].

$$\rho(E_{DL}-E_{AL}-\hbar\omega)=N\,exp\,\frac{-(E_A-E_D)}{K_BT} \text{ ....(2)}$$

Where $E_A and, E_D$ are the energy of

acceptor and donor state, k_B is the Boltzmann constant , ω is the frequency ,N is the normalized constant ,and T is the absolute temperature.

Note that the height barrier $\Delta G^{++}$for displaced harmonic oscillators is $\Delta G^{++}= E_A - E_D$, then the rate equation of electron transfer becomes.

$$R_{et}=\frac{2\pi}{\hbar}\ |T_{DA}|^2\ \rho(\Delta G^{++})\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(3)$$

However the height barrier ΔG^{++} could be estimated with the Marcus theory [10] .

$$\Delta G^{++}=\Delta G^{0++} - \frac{nF}{2}\ (\Delta\Phi - \Delta\Phi^0) + \frac{n^2F^2}{4E_0}(\Delta\Phi - \Delta\Phi^0)\ \ldots\ldots(4)$$

Where $\Delta G^{\circ++}$ is the height potential barrier (activation free energy) at equal the interfacial potential difference ($\Delta\Phi$=$\Delta\Phi$°), $\Delta\Phi$,and $\Delta\Phi$° are the redox potential for donor and acceptor state, n is the number of electrons ,F is the Faraday constant ,and E_0 is total reorganization energy. The height barrier energy of reaction can be expressed as [11].

$$\Delta G^{++}= -nf\ (\Delta\Phi- \Delta\Phi^\circ)\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(5)$$

And the height potential barrier from classical Marcus theory is given by [12].

$$\Delta G^{++}= \frac{E_0}{4} - \frac{\Delta G_0}{2} + \frac{G_0^2}{4E_0} = \frac{(E_0-\Delta G_0)^2}{4E_0}\ \ldots\ldots\ldots\ldots(6)$$

Where E_0 is contribution of the reorganization energy due to reaction ,and ΔG_0 is the driving force energy When the liquid/liquid system absorption photon light to excited and that's can be written as [13].

$$\Delta G_0 = (h\nu - E_0)\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(7)$$

Where ΔG_0 is the effective free energy (driving force)is given by [14].

$$\Delta G_0 = h(c/\lambda) - E_0\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(8)$$

Where $\hbar$, is Planck constant, ν is the frequency, c is the velocity of light and λ is the wave length. The reorganization energy E_0 due to electron transfer reaction at liquid/liquid system can be written as [15].

$$E_0 = \frac{(\delta e)^2}{4\pi\epsilon_0}\left[\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{R}\right]\left(\frac{1}{\epsilon_1^{op}+\epsilon_2^{op}} - \frac{1}{\epsilon_1^{S}+\epsilon_2^{S}}\right)\ldots\ldots\ldots\ldots\ldots(9)$$

Where $R = a_1 + a_2$ is the separation distance between the two reactants and a_1, a_2 are the radii of ions ,ϵ_1^{op} ,ϵ_2^{op} , ϵ_1^{S}, and ϵ_2^{S} refers to the optical static dielectric constant of two liquid respectively. The radii of donor and acceptor can be estimated from the apparent molar volume using spherical approach [16].

$$a_i = \left(\frac{3MW}{4\pi N_A \rho}\right)^{\frac{1}{3}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(10)$$

Where a_i is the radius of donor or acceptor, NA Avogadro's number constant , MW is the molecular weight, and ρ is the mass density of liquid.

Results

The calculation of the rate constant of charge transfer depends on three main terms that’s appearing in it; the reorganization energy, the electronic coupling, and the potential barrier height. The reorganization energy can be evaluated depending on the outer sphere model that is derived based on the electro statistics potential of the molecular donor and acceptor. The reorganization energy is needed to the reorientation of system before the transfer. The molecular parameters introduced in this model are the molecular weight MW, mass density ρ are taken from Table 1 and radius of molecule that’s evaluated according the apparent molar volume using spherical approach in Eq.(10),the results are summarized in Table 1. The reorganization energy for water / liquid system can be calculated using Eq.(9) with inserting the values of radii of donor and accepter from Table(1), and dielectric constant ϵ optical dielectric constant ϵ_{op} from Table (2) and assume the distance $R = a_D + a_A$ between center to center for donor and acceptor knowing that $(\frac{e^2}{4\pi\epsilon} = 14.4\ eV)$ the results of reorganization free energy have been summarized in Table (2) .

The second step is to calculate the driving force energy (free energy) term at the liquid/liquid interface as a function of the reorganization energy ,and the absorption energy . The energy changes for the drive free energy of the charge to transfer from donor to acceptor involved the difference between the reorganization energy and absorption spectrum energy Eq.(8). The results of the reorganization energy in Table 2 can then be used to find the values of a driving force energy and barrier potential. The absorption energy in Eq. (8) can be roughly taking from the wave length in visible spectrum(4000A°-7000A°) and transform energy equation $E = h\nu = \frac{hc}{\lambda}$,where h is Planck constant ,c is the velocity of light ,and λ is the wave length .

Since we have considered that the absorbed visible light is directed to the aqueous phase .we evaluated the driving force energy for liquid/liquid system by inserting the values of the reorganization energy from Table 2, and absorption energy from spectrum in Eq. (8), results are listed in Table 3.

The height potential barrier $\Delta G^{++}(eV)$ using Eq.(6), by inserting the results of both reorganization energy from Table (2),and driving force energy in Table(3), with Math lab program. The results are formulated in Table (4).

Discussion

In this paper we calculate the height potential barrier t $\Delta G^{++}(eV)$ for charge transfer at liquid/liquid interface system depending on the results of the reorganization energies and the driving free energy (driving force ΔG_0).

The height potential barrier $\Delta G^{++}(eV)$ have been tested the probability of the transfer of charge from donor water to liquid acceptor state. Table (2) show that the reorganization energy for charge transfer at liquid/liquid system increases with increasing of the dielectric constant for acceptor in the system ,also an increases in the refractive index for acceptor liquid leads to decrease in the reorganization energies for system with the same refractive index (n) and dielectric constant for the donor. This indicate that the reorganization energy as a function of the polarity for system. The small polarity function results to decreasing the reorganization energy and vice versa .

Also the effective radius $R \approx (a_1 + a_2)$ for the interface system reduce to $E^o \approx 0.6932973949\ (eV)$: $0.8986405084\ (eV)$ for water/liquid . Although this values for $E_0(eV)$ might seem reasonable, it must be emphasized that Eq. (9) constitutes an oversimplification, and more elaborate Marcus -Hush model for $E_0(eV)$ should be used for quantitative purposes. Table(3) gives the results of the driving force energy for charge transfer is take term accounting for the attractive interactions between the tails of the donor state wave function and acceptor state wave function. Calculated results of the driving force energy as a function of the reorganization energy and the absorption energy visible spectrum (4000A^o-7000 A^o) . Results in Table (3) of driving force ΔG_0(eV), show that the driving force energy take to bring the donor and acceptor together and it is the part of the work broken to derive the charge to transfer from donor to acceptor. The driving force energy to drive the charge increases with increasing of absorption energy and decreasing in wave length. Table 4 gives the theoretical height barrier ΔG^{++} (eV) at liquid/liquid interface that obtained with the semi classical Marcus model given in Eq.(6) for different liquid/liquid system. Height barrier $\Delta G^{++}(eV)$ decreases with the decreasing of the driving force energy and with the of increasing the absorption energies .This indicate that the absorption energy divided to reorientation.

The system to transfer and the other enable to drive the charge to transfer due to height potential barrier from donor to acceptor. The height barrier $\Delta G^{++}(eV)$ values calculated from this model agree also with those observed rate constant [9]. Again, the transition is so much small as when the barrier is large . In the low values of barrier ,the transfer of electrons are most probable from donor to accepter .The large height barrier exclusion transfer across liquid/liquid system and the electron suffering much resistant to transfer . However, this excluded transfer could be significantly lower for high barrier and small concentrations of charge because of the hard (large height) barrier overlapping effect ignored in Eq. (6).

Conclusions

In summary the results calculation of the height potential barrier for charge transfer at liquid/liquid interface system are function of the reorganization energies and the driving free energy (driving force). The reorganization energy $E_0(eV)$ in indicate that the charge transfer is more probable in liquid-liquid system have more polarity parameter Not ably the charge transfer in system have large dielectric constant are stronger than system have small dielectric constant. The driving force energy for charge transfer is take term accounting for the attractive interactions between the tails of the donor state wave function and acceptor state wave function and depending on the reorganization energy and the absorption energy visible spectrum. It energy that take to bring the donor and acceptor together and drive the charge increases with increases absorption energy and decreasing in wave length. height barrier ΔG^{++} (eV) at liquid/liquid interface that decreasing with decreasing the driving force energy and increasing the absorption energies

This indicate the absorption energy divided to reformation the system to transfer and the other enable to drive the charge to transfer due to potential barrier height from donor to acceptor. It can be concluded the transition is so much small as a barrier large values but in the low values of barrier, the transfer is most probable the large height barrier exclusion transfer across liquid/liquid system and the charger suffering much resistant to transfer .

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Table 1. The theoretical calculation values of radii a_i(A°) for water donor and acceptor liquid [17-18].

Liquid Type	**Molecule wt. (MW)$g.mol^{-1}$ [17-18]**	**Density (ρ) $g.cm^{-3}$ [17-18]**	**Calculated radii $a_i(A^0)$**

Water	18	1	1.92520792
Acetone	58.08	0.791	3.076121696
Formic acid	46.03	1.22	2.463847665
Bromoform	252.73	2.889	3.261043233
Chloroform	119.38	1.483	3.171881441
N-methylformamide	59.07	1.003	2.858087259
N,N dimethylformamide	73.09	0.944	3.13099322
Ethanol	46.0414	0.790	2.848135287
Haxanic acid	116.16	0.93	3.672073423
1,2 ethanediol	63	1.1151	2.818787796
n-hexadecane	226.44	0.733	4.96595975

Table 2. The reorganization free energy E_0 (eV) for charge transfer at water\liquid interface system.

Liquid Type	**Dielectric constant for acceptor ϵ_s[19-20]**	**Optical dielectric constant for acceptor ϵ_{op}[19-20]**	**Reorganization free energy E_0 (eV) [17-18]**
Water/Acetone	20.493	1.84633744	0.8516752339
Water/Formic acid	51.1	1.88073796	0.8986405084
Water/Bromoform	4.2488	2.56160025	0.6932973949
Water/Chloroform	4.7113	2.09062681	0.7858438989
Water/N,Methylformamide	181.59	2.05033761	0.8363805396
Water/N, Ndimeethylformamide	37.219	2.04633025	0.8075301745
Water/Ethanol	24.852	1.85259321	0.8635918533
Water/n-hexadecane	2.0402	2.05779025	0.8246426859
Water/Hexanic acid	2.6	2.00590569	0.8118435171
Water/1,2 Ethanediol	40.245	2.05005124	0.8244227082

Table 3. The driving force energy $\Delta G_o(eV)$for charge transport in water/liquid system.

	Driving force energy $\Delta G_o(eV)$

Wave length λ (A°)	**Water-Bromoform**	**Water-n-hexadecane**	**Water-Chloroform**	**Water-N,Ndimethylformamid**	**Water-Haxanic acid**	**Water-1,2ethanediol**	**Water-n-methylformamide**	**Water-Acetone**	**Water-Ethanol**	**Water-Formic acid**
4000	2.4127	2.2813	2.3201	2.2984	2..2941	2.2815	2.2696	2.2543	2.2424	2.2073
4500	2.0676	1.9362	1.9750	1.9533	1.9490	1.9364	1.9245	1.9092	1.8973	1.8622
5000	1.7915	1.6601	1.6989	1.6772	1.6729	1.6603	1.6484	1.6331	1.6212	1.5861
5500	1.5656	1.4342	1.4730	1.4513	1.4470	1.4344	1.4225	1.4072	1.3953	1.3602
6000	1.3774	1.2460	1.2848	1.2631	1.2588	1.2462	1.2343	1.2190	1.2071	1,1720
6500	1.2181	1.0867	1.1255	1.1038	1.0995	1.0869	1.0750	1.0597	1.0478	1.0127
7000	1.0816	0.9502	0.9890	0.9673	0.9630	0.9504	0.9673	0.9232	0.9113	0.8762

Table 4. The results of height potential barrier $\Delta G^{++}(eV)$ for charge transport at water/liquid interface system.

Wave length $\lambda\ (A^o)$	**Height Barrier $\Delta G^{++}(eV)$**									
	Water-Bromoform	**Water-n-hexadecane**	**water-Chloroform**	**Water-N,N dimethylformamide**	**Water-Haxanic acid**	**Water-1,2 ethanediol**	**Water-N,methylformamide**	**Water-Acetone**	**Water-Ehanol**	**Water-Formic acid**
4000	3.4790	2.9246	3.0790	2.9865	2.9707	2.9253	2.8837	2.8315	2.7928	2.6837
4500	2.7488	2.3108	2.4249	2.3597	2.3472	2.3113	2.2784	2.2372	2.2067	2.1205
5000	2.2265	1.8717	1.9641	1.9113	1.9012	1.8721	1.8455	1.8121	1.7874	1.7175
5500	1.8400	1.5468	1.6232	1.5796	1.5712	1.5472	1.5252	1.4976	1.4771	1.4194
6000	1.5462	1.2998	1.3640	1.3273	1.3203	1.3001	1.2816	1.2584	1.2412	1.1927
6500	1.3174	1.1075	1.1622	1.1309	1.1249	1.1077	1.0920	1.0722	1.0576	1.0163
7000	1.1360	0.9549	1.0021	0.9750	0.9700	0.9552	0.9416	0.9245	0.9116	0.8763