Theory and Calculation of the Reorganization Energy of Electron Transfer at Liquid/Liquid Interface

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Abstract

A description of the theoretical of the reorganization energies have been described according to the outer-sphere Marcus model .It is a given expression according this model unable to evaluate the reorganization energy for electron transfer at liquid /liquid interface. The spherical model approach have been used to evaluate the radius of donor and acceptor liquid alternatively .Theoretical results of the reorganization free energy for electron transfer at liquid/liquid interface system was carried out . Matlap program is then used to calculate E_0 for electron transfer reaction between water donor stated and many liquid acceptor state. This shows a good agreement with the experiment. The results calculation shows that E_0 is a function of dielectric constant and refractive index and polarity of acceptor .

Key word: Reorganization energy, Electron transfer, liquid/liquid interface.

Introduction

Electron transfer (ET) reaction is one of the most fundamental processes in chemistry and biology. Both experiment and theory calculation of electron transfer (ET) have made tremendous progress [1] .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[2] . In simple terms, an electron transfer (ET) reaction involves the transfer of an electron from a 'donor' to an 'acceptor'[3].Since no chemical bonds are broken or formed in the transfer and further more the changes in the bond lengths and angles are rather small[4] . Electron transfer (ET) reaction involves an oxidation of donor $|D>$ state and reduction of an acceptor $|A>$ state are among the most significant and universal processes[5]. The electron donor acceptor molecules play a key role in understanding the charge transfer processes[6].The effect of a solvent on the kinetics of (ET) reaction is controlled by coupling of the electric charge of the transferred electron to the nuclear component of the electric potential created by the partial charges on the overall natural solvent molecules [7].One of the most important factor on electron transfer reaction is the reorganization energy $E_0(eV)$ that is defined as the charge in energy if the reactant state $|D>-|A>$ were to distort to equilibrium configuration of the product state $|D^+>-|A^->$ without transfer of the electron [8].Despite the importance of $E_0(eV)$ in the electron transfer kinetics precise measurement of this quantity are rather rare as it is difficult to measure the reorganization energy directly [9]. The charging path is use to produce a system with a non equilibrium dielectric polarization to obtain statistical mechanical expression for the free energy of a system [10].In this paper, we will study the reorganization energy one of the most important parameters of the charge transfer in liquid/liquid interface with outer-sphere model according the electrostatic potential. Many acceptor liquids are used with water donor to calculate the value of reorganization energies.

Theory

The Marcus description of outer-sphere electron transfer reaction has been extensively studied for electron transfer between molecular electron acceptor$|A>$ and donor $|D>$ species in solution [11].We assume the electron transfer processes that are obtained between a reactant one liquid donor $|D>$state and a reactant immiscible liquid acceptor $|A>$state system as illustrated in scheme 1.

$$|D>(liq1)+|A>(liq2)\overset{ET}{\rightarrow}|A^->(liq1)+|D^+>(liq2)$$

Under anon equilibrium of the two reactant system in a fixed position with a charge distribution ρ and a distance R between their center. Frist assumes that two dielectric liquid as a plane interface at Z=0,and electron is a fixed at d form interface [10].

The electrostatic potential is generated at any point distant r from the center of the ion is given by .

$$\Phi_{(r)}=\frac{e}{4\pi\in_0\in_s r}\ \ldots\ldots\ldots\ldots\ldots\ldots..\ (1)$$

The work required to charge the ion in dielectric solvent from (0 to e_0) is

$$W=-\int_0^{e_0}\Phi_{(r)}de=\frac{-e_0^2}{8\pi\in_0\in_s r}\ \ldots\ldots\ldots\ldots\ldots\ldots..\ (2)$$

For linearity medium to a charge in electric field and static treatment low frequency of electronic polarization in the system .When a solvent nuclear coordinates are fixed , but allowing the electronic polarization of solvent a adapted , then the charge that determines the distribution of coordinates in the transition state e_{ET} is to be given [13].

$$e_{ET}=e_0+\lambda(e-e_0)\ \ldots\ldots\ldots\ldots\ldots\ldots..\ (3)$$

Where λ is the lagrangian coefficient ,then the potential in Eq.(1) can be written as.

$$\Phi_{(r)}=\frac{e_0}{4\pi\epsilon_0\epsilon_s r}+\frac{\lambda(e-e_0)}{4\pi\epsilon_0\epsilon_{op}r}\ \ldots\ldots\ldots\ldots\ldots\ldots..\ (4)$$

Where $\epsilon_s$and ϵ_{op} are the static and optical dielectric constant. The change in charge is the electronic polarization of the solvent and optical dielectric constant then the work required to change the ion in dielectric solvent is to be written as [13] .

$$W_T = \int_{\lambda=0}^{1} \Phi_{(r)} de_{ET} = \int \left(\frac{e}{4\pi\epsilon_0\epsilon_s r} + \frac{\lambda(e-e_0)}{4\pi\epsilon_0\epsilon_{op} r} \right) de_{ET} = \frac{e(e\_e_0)}{4\pi\epsilon_0\epsilon_s r} + \frac{(e-e_0)^2}{8\pi\epsilon_0\epsilon_{op} r} \dots\dots\dots\dots\dots\dots (5)$$

The work done to the change of the a actuation solvent is

$$W_{act} = \frac{e_0^2}{8\pi\epsilon_s\epsilon_{op} r} \dots\dots\dots\dots\dots\dots (6)$$

Then the energy of solvent that describe the non equilibrium dielectric polarization in the liquid /liquid system is given by adding Eq. (5) and Eq. (6) with Eq. (2), results.

$$\Delta E = \frac{e_0^2}{8\pi\epsilon_s\epsilon_0 r} + \frac{e\,(e-e_0)}{4\pi\epsilon_0\epsilon_s r} + \frac{(e-e_0)^2}{8\pi\epsilon_0\epsilon_{op} r} - \frac{e_0^2}{8\pi\epsilon_s\epsilon_0 r} \dots\dots\dots\dots\dots\dots (7)$$

Simply to

$$\Delta E = \frac{(e-e_0)^2}{8\pi\epsilon_0 r} \left(\frac{1}{\epsilon_{op}} - \frac{1}{\epsilon_s} \right) \dots\dots\dots\dots\dots\dots (8)$$

For a non equilibrium liquid-liquid interface the actual charge can be given as [14].

$$e_{0,1} = e_1 + m\left(e_1 - e_1^p\right) = e_1 - m\Delta e \dots\dots\dots\dots\dots\dots (9)$$

$$e_{0,2} = e_2 + m\left(e_2 - e_2^p\right) = e_2 + m\Delta e \dots\dots\dots\dots\dots\dots (10)$$

With Eq.(8),the energy of solvation for two ions is given by

$$\Delta E^{noneq} = \frac{1}{4\pi\epsilon_0} \left[\frac{(e_1-e_{01})^2}{2a_1} + \frac{(e_2-e_{02})^2}{2a_2} - \frac{(e_1-e_{01})(e_2-e_{02})}{a_1+a_2} \right] \left[\frac{1}{\epsilon_{op}} - \frac{1}{\epsilon_s} \right] \dots\dots\dots\dots\dots\dots (11)$$

We then obtain at a fixed position the reactant [15].

$$\Delta E^{noneq} = \lambda^2 E_0 \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots \dots .. (12)$$

Where E_0 is the contribution of the solvent reorganization energy due to reaction by comparing Eq. (11), and Eq. (12) ,E_0 can be written as.

$$E_0 = \frac{(\Delta e_0)^2}{4\pi\epsilon_0} \left[\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{a_1+a_2} \right] \left[\frac{1}{\epsilon_{op}} - \frac{1}{\epsilon_s} \right] \dots\dots\dots\dots\dots\dots (13)$$

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_{op} and ϵ_s refers to the optical and static dielectric constant of two liquids and given by [15].

$$\epsilon_{op} = \epsilon_{op1} + \epsilon_{op2} \dots\dots\dots\dots\dots\dots (14)$$

$$\epsilon_s = \epsilon_{s1} + \epsilon_{s2} \dots\dots\dots\dots\dots\dots (15)$$

Substituting Eq. (14) and Eq.(15) in Eq. (13) results.

$$E_0 = \frac{(\Delta e)^2}{4\pi\epsilon_0} \left[\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{R} \right] \left(\frac{1}{\epsilon_1^{op} + \epsilon_2^{op}} - \frac{1}{\epsilon_1^S + \epsilon_2^S} \right) \dots\dots\dots\dots\dots\dots (16)$$

The radii of donor and acceptor can be estimated from the apparent molar volume using spherical approach [16].

$$a_i = \left(\frac{3MW}{4\pi N_A \rho} \right)^{\frac{1}{3}} \dots\dots\dots\dots\dots\dots (17)$$

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

Results

For the liquid/liquid interface systems ,one of the most important parameter for charge transfer is the reorganization free energies $E_0(eV)$.This can be calculation of theoretically by using the expression(15).The calculate the values of the reorganization energies$E_0(eV)$ for water/liquid system, one can find the values of radius for donor (water) and acceptor (liquid) using Eq.(16),substation the values of Avogadro's construes $NA = 6.02 \times 10^{23} \frac{Molecule}{mol}$, molecular weight MW ,and Density mass ρ for all liquids from table (1) in Eq. (16) we can evaluate the theoretical values of radii for water and variety of liquid , values of this calculation one are listed in the table (2) .

Next we can calculate the reorganization free energy for water / liquid system by inserting in expression (15) the values of radii of donor and accepter , dielectric constant ϵ optical dielectric constantϵ_{op} from table (1) and assume the distance $R = a_D + a_A$ between center to center for donor and acceptor knowing that $\frac{e^2}{4\pi\epsilon_0} = 14.4\ eV$ the results of reorganization free energy have been summarized in table (3).

Discussion

In our research ,we have been applied the semi classical treatment to calculate the reorganization free energies for charge transfer at liquid/liquid interface system using a two spherical model based on the Marcus theory of electron transfer (ET) .The results of the reorganization energy for liquid/liquid system indicate that is in general whenever there is an increase in the dielectric constant for acceptor, there is an increase in the reorganization energies,similary whenever, there is an increase in the interface index for acceptor liquid leads to decrease in the reorganization energies for system with the same refractive index and dielectric constant for the donor .This can be explained from the physical meaning of the reorganization energy that is usually assumed comprise two contributions from the inner molecule and the oriented molecule dipoles lead to say the change transfer interaction for donor with acceptor molecule which results from the reorganization energy. The more range dielectric constant for acceptor reduce the reorientation of the donor molecule about acceptor needed more energy.It has been observed from table (3) that when the refractive index of acceptor molecule is large leads to small energy to reorganizefor system.

Also one of the most effect on the reorganization energy is the polarity function $f(n,\epsilon) = \left(\frac{1}{\epsilon_{op}} - \frac{1}{\epsilon_s}\right)$ for system, the small polarity function results to decrease the reorganization energy. Table (3) shows that when the acceptor liquid oil more polar leads to have large value of the reorganization energy this because of the type of oil has large dielectric constant that shows for Dodecanese($\epsilon_{s\approx}2.5$) has range value of ($E_0 = 0.778\ eV$),while the Decalin oil has small dielectric constant $\epsilon_s = 2.196$ that leads to small value of $E_0 \approx 0.700\ eV$.On the other hand the reorganization energy for the system contains oil has large refractive index leads to small value for reorganization energy such that Idobenzene $n = 1.62$ event has large dielectric constant $\epsilon_s = 4.5$ this indicates that the effect of total polarity term .In summary the results of calculation of the reorganization energy E_0 in table (3),indicate that the charge transfer is more probable in liquid-liquid system has more polarity parameter for example water/formic acid have $f(n,\epsilon) \cong 0.2657$ lead to large reorganization energy $E_0 \approx 0.898\ eV$.Not ably the charge transfer in system has large dielectric constant are stronger than system have small dielectric constant. Our results show agreement with experimental value for E_O [12].

Conclusions

It can be summarized depending the our results of calculation that the charge transfer is more probable happen and stronger depends on the three parameters dielectric constant, optical properties (refractive index)and polarity .It has shown that all donor molecular have large dielectric constant ,has large reorganization energies for charge transfer ,indicate that the transitions involve more energy to happen .On the other hand the increase of refractive index leads to small depending on the optical properties of molecule. Consequently the system has large E_0 refers that type of oil has more reaction media than other oil types with same donor.

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Table(1):Characteristic of Liquid Material

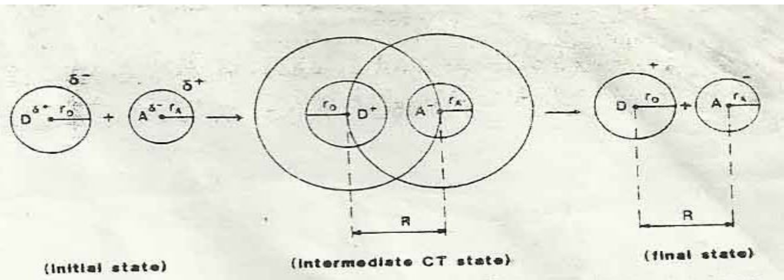
Liquid Type	Molecule weight (MW) $(g.mol^{-1})$ [17,19]	Density(ρ) $(g.cm^{-3})$ [17,19]	Dielectric constant (ϵ_s) [20,21]	Refractive index(n) [20,21]
water	18	1	80	1.333
Acetone	58.08	0.791	20.493	1.3588
Dodecane	170.33	0.750	2	1.421
Decalin	138.25	0.896	2.196	1.47553
Formic acid	46.03	1.22	51.1	1.3714
Bromoform	252.73	2.889	4.2488	1.6005
Chloroform	119.38	1.483	4.7113	1.4459
Cyclohexane	84.16	0.779	2.0165	1.4266
Perfluorobenzene	186.05	1.6120	2.029	1.3777
N-methylformamide	59.07	1.003	181.59	1.4319
N,N dimethylformamide	73.09	0.944	37.219	1.4305
Ethanol	46.0414	0.790	24.852	1.3611
n-hexadecane	226.44	0.733	2.0402	1.4345
Idobenzene	204.01	1.831	4.5470	1.6200
Cumene	120.19	0.862	2.3712	1.4912
Mesitylene	120.19	0.8637	2.2650	1.4994
Haxanic acid	116.16	0.93	2.6	1.4163
1,2 ethanediol	63	1.1151	40.245	1.4318
m-xylene	106.16	0.86	2.3478	1.4972

Table (2):The theoretical calculation values of radii $a_i(A^\circ)$ for donor and acceptor liquids

Liquid Type	Molecule weight (MW) $(g.mol^{-1})$ [17,19]	Density (ρ) $(g.cm^{-3})$ [17, 19]	Radii $a_i(A^0)$
water	18	1	1.92520792
Acetone	58.08	0.791	3.076121696
Dodecane	170.33	0.750	4.481913106
Decalin	138.25	0.896	3.940087332
Formic acid	46.03	1.22	2.463847665
Bromoform	252.73	2.889	3.261043233
Chloroform	119.38	1.483	3.171881441
Cyclohexane	84.16	0.779	3.498723009
Perfluorobenzene	186.05	1.6120	3.576638252
N-methylformamide	59.07	1.003	2.858087259
N,N dimethylformamide	73.09	0.944	3.13099322
Ethanol	46.0414	0.790	2.848135287
n-hexadecane	226.44	0.733	4.96595975
Idobenzene	204.01	1.831	3.534878643
Cumene	120.19	0.862	3.809258931
Mesitylene	120.19	0.8637	3.806758065
Haxanic acid	116.16	0.93	3.672073423
1,2 ethanediol	63	1.1151	2.818787796
m-xylene	106.16	0.86	3.657696142

Table(3):Our calculation results of reorganization free energy $E_0\ (eV)$ for charge transfer at water/liquid interface system.

System Type	Dielectric constant ϵ_s for acceptor [19-20]	Optical dielectric constant ϵ_{op} for acceptor	Reorganization free energy $E_0(\ eV)$
Water/Acetone	20.493	1.84633744	0.8516752339
Water/Dodecanese	2	2.019241	0.778518135
Water/decalin	2.196	2.177188781	0.7002127746
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/cyclohexane	2.0165	2.03518756	0.7861255431
Water/perfluorobenzene	2.029	1.89805729	0.8150156249
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/Idobenzene	4.5470	2.6244	0.6761547218
Water/Cumene	2.3712	2.22367744	0.7415657842
Water/Mesitylene	2.2650	2.24820036	0.7369760191
Water/hexanic acid	2.6	2.00590569	0.8118435171
Water/1,2 ethanediol	40.245	2.05005124	0.8244227082
Water/m-xylene	2.3478	2.24160784	0.7406532221



Initial state **Intermediate CT state** **Final state**

Fig.(1): Solute-solvent cage charge transfer complex model for an electron-transfer reaction between a redox reactant pair. Donor D and acceptor A.

الحسابات النظرية لطاقة اعادة الترتيب للانتقال الالكتروني لسطح سائل/سائل

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الخلاصة

وصفت طاقة اعادة الترتيب تبعا لانموذج ماركوس الكروي.استخدمت علاقة تبعاَ لهذا الانموذج تمكنا بها من حساب طاقة اعادة الترتيب للانتقال الالكتروني لسطح سائل/سائل . استعمل انموذج التقريب الكروي لحساب نصف القطر للسائل الواهب والقابل على التتابع.النتائج النظرية للطاقة الحرة لاعادة الترتيب للانتقال الالكتروني لسطح نظام سائل/سائل اجريت. ببرنامج الماتلاب الذي استعمل لحساب طاقة اعادة الترتيب(E_0) التفاعل الانتقال الالكتروني مابين حالة الواهب (الماء) وحالة المستقبل للسوائل المختلفة، نتائج الحسابات اظهرت توافقاً جيداً مع العملي،النتائج المحسوبة بينت ان (E_0) دالة ثابت العزل الكهربائي ومعامل الانكسار والاستقطابية للقابل.

الكلمات المفتاحية:طاقة اعادة الترتيب، الانتقال الالكتروني،سطح سائل/سائل.