DETERMINATION OF TRANSFER COEFFICIENT THROUGH MEAN EXIT TIME METHOD FOR MODEL POTENTIALS

A Thesis Submitted to the School of Graduate Studies
Addis Ababa University

In Partial Fulfilment of the Requirements for the
Degree of Master of Science in Physics

By
Dawit Solomon

Addis Ababa, Ethiopia
July 2006

ADDIS ABABA UNIVERSITY
FACULTY OF SCIENCE
DEPARTMENT OF PHYSICS

The undersigned hereby certify that they have read and recommend to the Faculty of Science School of Graduate Studies for acceptance a thesis entitled "**Determination of transfer coefficient through mean exit time method for model potentials**" by ***Dawit Solomon*** in partial fulfillment of the requirements for the degree of **Master of Science in Physics**.

Dated: July 2006

Name	Signature
Dr. Mulugeta Bekele, Advisor	_______________
Dr. Mesfin Asfaw, Examiner	_______________
Dr. S. K. Ghoshal, Examiner	_______________

"Thanks to all My Family"

Acknowledgements

From the very beginning, I would like to thank the Almighty God who brought me into picture. Wishing him a God blessing, I would like to truly express my deepest gratefulness to my advisor and instructor Dr. Mulugeta Bekele for his non-stopping guidance to a blend of physics, assistant and follow up, during carrying out the course and thesis work. I really admire him for his friendly approach with immeasurable and valuable contribution throughout the whole period of the research work.

I am very much pleased to thank for the rewarding discussion with Proff. Tewodros Solomon and Dr. Shimeles Demissie, regarding the theoretical aspects of this thesis.

It is my heartily desire to address enormous pleasure to Dr. Mesfin Asfaw for his sharing ideas and check over my thesis.

It gives me pleasure to acknowledge Awassa University for the sustainable financial hold up I received during my study.

My parents should take their share of my boundless gratification. I have special heart for my mom who really feels my busyness and provides me all my requirements. Eventually, thanks be to my friends for all kinds of encouragement and support I get from them.

Dawit Solomon
July, 2006
Addis Ababa.

Abstract

The electrochemical oxidation of the Activated Complex (AC) has shown very low (0.1) values of Anodic Transfer Coefficient (ATC) for conducting polymers such as Polypyrrole and Polyaniline [2-5] a particular model potential barrier. In order to explain the cause for such low values of ATC, Aoki used a specific potential hill to estimate such low value for the ATC. He used Langevin dynamics to describe the motion of the AC. In our present work, using the method of finding mean exit time, we are able to get expressions of the ATC for three model potential hills where one of the model we took is approximately that of Aoki's potential hill. Depending on the parameters of the model potentials, we have explored the conditions under which the ATC value goes from 0.5 to as small as 0.1 or less. Eventhough, the method we used to get the expression for the ATC is completely different from that used by Aoki, we are able to get very low values of ATC under highly asymmetric conditions of the model potential hills.

Table of Contents

Table of Contents **vi**

List of Figures **viii**

1 Introduction **2**

2 Kinetics of Electrode Reaction **6**

- 2.1 Essentials of Electrode Reactions 6
- 2.2 Butler-Volmer Model of Electrode Kinetics 8
  - 2.2.1 One-step, One-Electron process 8
  - 2.2.2 Basic concepts about the Transfer Coefficient 13
  - 2.2.3 Derivation for Transfer Coefficient 15
  - 2.2.4 The Tafel equation 16

3 Dynamics of an activated complex in an asymmetric potential profile **17**

- 3.1 The activated complex in asymmetric potential 17
- 3.2 Calculation of mean exit time and anodic transfer coefficient 19
  - 3.2.1 Probability of exit time through a particular end of the interval 20
  - 3.2.2 Calculation of mean velocity and transfer coefficient 24

4 Determination of the mean exit time and anodic transfer coefficient for model potentials **26**

4.1 Mean exit time from $x = 0$ to $x = a$ and from $x = 0$ to $x = b$ for first model potential . . . 29
4.2 Mean exit time from $x = 0$ to $x = a$ and from $x = 0$ to $x = b$ for second model potential . . . 30
4.3 Mean exit time from $x = 0$ to $x = a$ and from $x = 0$ to $x = b$ for third model potential . . . 32
4.4 Result and Discussion . . . 34
    4.4.1 Analytical and Numerical results for first model potential . . . 34
    4.4.2 Numerical results for second model potential . . . 38
    4.4.3 Analytical result for third model potential . . . 39

5 Summary and Conclusion 42

A Appendix 43

Bibliography 44

List of Figures

1.1 A sketch of a typical reaction profile. 3

1.2 Potential profile for the electrode reaction of a conducting polymer from the neutral (insulating) state to the doped (conducting) state along the reaction coordinate. 4

2.1 Effects of a potential change on the standard free energies of activation for oxidation and reduction through Anodic and Cathodic direction along reaction coordinate. 9

3.1 Potential profile for the activated complex along a reaction coordinate. 18

4.1 Plot of two linearly connected potential hill with the activated complex placed at the top of the reaction coordinate. 27

4.2 Plot of an inverted parabolic potential hill with the activated complex placed at the top of the reaction coordinate. 27

4.3 Plot of three linearly connected potential hill with the activated complex placed at the top of the reaction coordinate. 28

4.4 Plot of $T(a,0)$ versus b analytically for some U_0(U1= $1k_BT$, U2= $2k_BT$ and U3= $4k_BT$). 35

4.5 Plot of $T(a,0)$ versus b numerically for some U_0(U1= $1k_BT$, U2= $2k_BT$ and U3= $4k_BT$). 35

4.6 Plot of $T(b,0)$ versus b analytically for some U_0(U1= $1k_BT$, U2= $2k_BT$ and U3= $4k_BT$). 36

4.7 Plot of $T(b,0)$ versus b numerically for some U_0(U1= $1k_BT$, U2= $2k_BT$ and U3= $4k_BT$). 36
4.8 Plot of anodic transfer coefficient versus b analytically for some U_0=$1k_BT, 2k_BT$ and $4k_BT$ but the graphs overlapped on each other. 37
4.9 Plot of anodic transfer coefficient versus b numerically for some $U_0 = 1k_BT, 2k_BT$ and $4k_BT$ but the graphs overlapped on each other. 38
4.10 Plot of $T(a,0)$ versus b for some U_0(U1= $1k_BT$, U2= $2k_BT$ and U3= $4k_BT$). 39
4.11 Plot of $T(b,0)$ versus b for some U_0(U1= $1k_BT$, U2= $2k_BT$ and U3= $4k_BT$). 40
4.12 Plot of anodic transfer coefficient versus b for $U_0 = 1k_BT, 2k_BT$ and $4k_BT$ but the graphs overlapped on each other. 41
4.13 Plot of anodic transfer coefficient versus α for $U_0 = 15k_BT$. 41

Chapter 1

Introduction

In Chemistry an Activated Complex (AC) is a translational structure in a chemical reaction which results from an effective collision between molecules and persists while old bonds are breaking and new bonds are forming. It is therefore a range of molecular geometries along the reaction coordinate.

In the AC theory, we consider two reactants approaching each other due to their potential energy rises and reaches a maximum value when the AC is formed. This is illustrated in Fig. 1.1. In this brief interval of bond breakage and bond formation, the collision complex is in a translational state. When molecules collide, some of their total kinetic energy is converted into potential energy within the colliding molecules. If enough energy is converted, the old bonds become sufficiently distorted for the colliding molecules to form an AC. New bonds can then begin to form.

According to the electrochemical reaction, there is usually a potential difference between two electrodes determining a tendency for the reaction to occur either to the product (oxidation) state or to the reactant (reduction) state. To quantify these competing tendencies a term called *transfer coefficient* is introduced to describe whether the reaction goes to forward or backward direction. This transfer coefficient divides into two terms which are defined as Anodic Transfer Coefficient (ATC) and Cathodic Transfer Coefficient (CTC). The ATC is defined by the probability for the AC to go

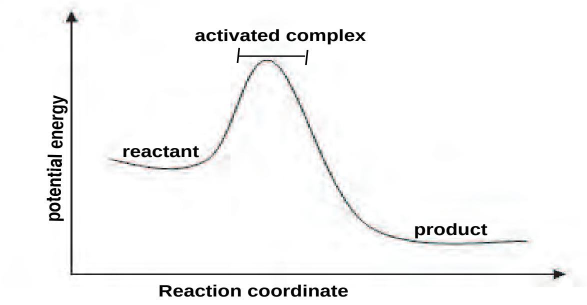

Figure 1.1: A sketch of a typical reaction profile.

to the product (oxidation) state while the CTC is defined by the probability of the AC to go to the reactant (reduction) state.

When there is no potential difference between the electrodes, one usually gets the transfer coefficient to be approximately around 0.5 which corresponds to the AC to have equal probability to go either to the reactant or product side. Such situation corresponds to the case where the potential profile around the barrier top to be symmetric. However, there are some chemical reactions where the value of the transfer coefficient is either close to zero or to unity. Recently it was reported that the electrochemical oxidation of electronically conducting polymers such as Polypyrrole and Polyaniline showed values of the ATC close to 0.1 which is an extraordinarily small in comparison to the conventional values close to 0.5 [2-5]. This corresponds to the case where the potential profile describing the reaction to be highly asymmetric. Using Langevin dynamics for the movement of the AC in an asymmetric activation energy hill as shown in Fig. 1.2, Aoki [1] expressed the transfer coefficient in terms of the thermal fluctuation of the conductance and the current density. The result he got was consistent with the experimental results.

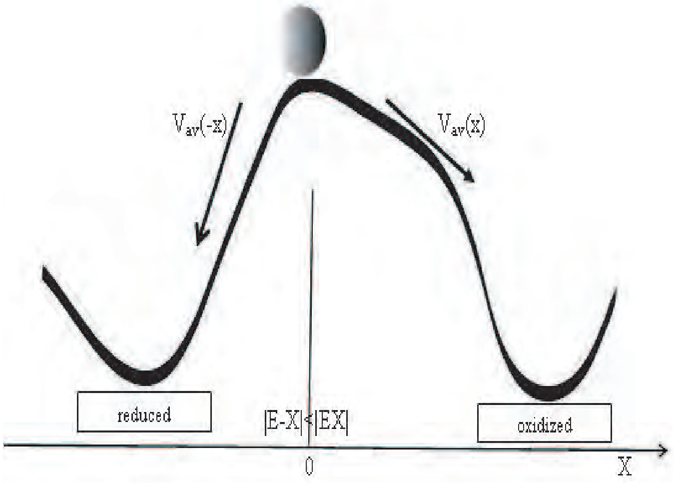

Figure 1.2: Potential profile for the electrode reaction of a conducting polymer from the neutral (insulating) state to the doped (conducting) state along the reaction coordinate.

The aim of this work is to find an alternative way of evaluating the ATC. We start by representing the ATC as the ratio of the velocity of the AC to go to the forward direction to that of the sum of the velocities for the AC to go to the forward and backward directions. By placing the AC at the potential maximum of the activation potential hill, we setup a method to determine the Mean Exit Times (MET) for the AC to reach either the product or reactant states. This will then enable us to evaluate the ATC. Taking particular models for the activation potential hills including the one approximately similar to that of Fig. 1.2, we evaluate the ATC for different parameter values of the model potential hills and explore the conditions under which its value goes from 0.5 to as small as 0.1 or less.

In short, we organize our work as follows. In Chapter 2, we introduce the kinetics of electrode reaction for one-step, one-electron process and derive an expression for the ATC using Butler-Volmer equation. In Chapter 3, we present our method of finding the MET essential to determine ATC for the AC. In Chapter 4, we use three particular model potentials to find the MET and then ATC. To do the calculation we use the method presented in Chapter 3 for three model potentials. We give both the analytical and numerical results for two of the three models but give numerical result only for the second model potential barrier because it is not solvable analytically. The last Chapter is devoted to summary and conclusions.

Chapter 2

Kinetics of Electrode Reaction

The main purpose of this chapter is to introduce the electrochemical kinetics. Let us now we consider the one - electron oxidation of a p-doped conducting polymer: $R(insulator) \longleftrightarrow O(conductor) + e^-$.

Here R is the neutral and electrically insulating species, and O is the doped and electrically conducting species. The activated complex here is defined as an intermediate state between $R(insulator)$ and $O(conductor)$. Once the oxidation proceeds at the interface between the conducting and insulating zone, the oxidized species is captured in the conducting zone, leading to the development of the front of the conducting zone.

When the activated complex is at the top of the reaction potential profile, the feasibility of the complex moving to the reactant side or the product side depends on the external forces (f) acting on the complex. In order to evaluate the probability of moving towards each side, our approach is to use Langevin equation: $f = -V'(x)$.

2.1 Essentials of Electrode Reactions

For an electrode reaction, equilibrium is characterized by the Nernst equation, which links the electrode potential to the bulk concentrations of the participants. In the general case:

$$Red \rightleftharpoons Ox + ne^{-}. \tag{2.1}$$

The above relation can be expressed like this,

$$E = E^{0} + \frac{RT}{nF} ln(\frac{C_{ox}^{*}}{C_{red}^{*}}), \tag{2.2}$$

where C_{ox}^{*} and C_{red}^{*} are the bulk concentrations, and E^{0} is the formal potential. Any valid theory of electrode kinetics must predict this result for corresponding conditions. We also require that the theory explain the observed dependence of current on potential under various circumstances. Early studies of such systems showed that the current is often related exponentially to the overpotential η, that is,

$$i = a^{'} e^{\eta / b^{'}}, \tag{2.3}$$

or, as given by Tafel in 1905,

$$\eta = a + blogi. \tag{2.4}$$

A successful model of electrode kinetics must explain the frequent validity of the Eq. (2.4), which is known as the *Tafel equation.* Let us begin by considering the reaction Eq. (2.1) has forward and backward paths as shown in Fig. 2.1. The forward component proceeds at a rate, υ_f, that must be proportional to the surface concentration of R. We express the concentration at distance x from the surface and at time t as $C_{red}(x,t)$; hence the surface concentration is $C_{red}(0,t)$. The forward reaction rate to $C_{red}(0,t)$ is the rate constant k_f,

$$\upsilon_f = k_f C_{red}(0,t) = \frac{i_a}{nFA}, \tag{2.5}$$

since the forward reaction is an oxidation, there is an anodic current, i_a, proportional to υ_f, likewise, we have for the backward reaction

$$\upsilon_b = -k_b C_{ox}(0,t) = -\frac{i_c}{nFA}, \tag{2.6}$$

where i_c is the cathodic component to the total current. Thus the net reaction rate is

$$\upsilon_{net} = \upsilon_f + \upsilon_b = k_f C_{red}(0,t) - k_b C_{ox}(0,t) = \frac{i}{nFA}, \tag{2.7}$$

and we have overall

$$i = i_a + i_c = nFA\big[k_f C_{red}(0,t) - k_b C_{ox}(0,t)\big]. \tag{2.8}$$

Note that heterogeneous reactions are described differently than homogeneous one. Since the interface can respond only to its immediate surroundings, the concentrations entering rate expressions are always surface concentrations, which may differ from those of the bulk solution.

2.2 Butler-Volmer Model of Electrode Kinetics

Experience demonstrates that the potential of an electrode strongly affects the kinetics of reaction occurring on its surface. In this section, we will develop a predictive model based purely on classical concepts. Even though it has significant limitations, it is very widely used in the electrochemical literature. Now we will see the one-step electrode reaction.

2.2.1 One-step, One-Electron process

Let us now consider the simplest possible electrode process, where in species O and R engage in a one-electron transfer at the interface without being involved in any other chemical steps [6],

$$R \rightleftharpoons O + e^-. \tag{2.9}$$

Charge transfer between reduced and oxidized state always proceeds via an activated intermediate complex. The height of the potential barrier depends on the electrode potential E. In the following pictures, the potential is shifted from the equilibrium value to a more positive potential. Note: only the state corresponding to the electrons in the metal is affected by the potential shift. An increase in E favors the anodic direction (oxidation) and disfavors the cathodic direction (reduction).

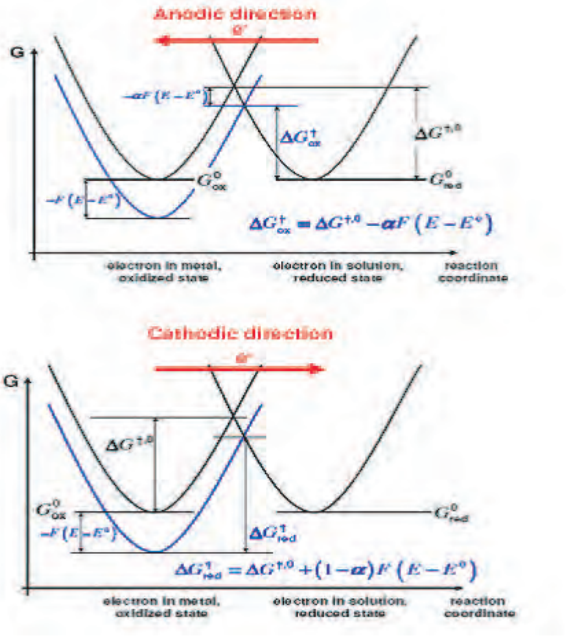

Figure 2.1: Effects of a potential change on the standard free energies of activation for oxidation and reduction through Anodic and Cathodic direction along reaction coordinate.

For any type of electrode reaction in solution, the Arrhenius expression relates the activation energy, $\Delta G^\ddagger$, with the rate constant, k:

$$k = Aexp[-\Delta G^\ddagger/RT], \tag{2.10}$$

now, the trends of changing the potential E are obvious:

$*$ For larger E and $\triangle G^{\ddagger}_{ox}$ smaller then anionic reaction faster, in other words: at larger electrode potential, electrons are more easily transferred from the solution to the metal.

$*$ For smaller E and $\triangle G^{\ddagger}_{ox}$ smaller then cathodic reaction faster, in other words: at larger electrode potential, electrons are more easily transferred from the metal to the solution. If the potential change by ΔE at E, the relative energy of the electrode resident on the electrode charges by $F\Delta E = -F(E - E^0)$, i.e., the $O + e^-$ moves up and down by that amount. From this $\Delta G^{\ddagger}_{ox}$ becomes less than $\Delta G^{\ddagger 0}$ by a fraction of a total energy change as shown in Fig. 2.1. Let us call that fraction α_T, where α_T, the *transfer coefficient*, can range from zero to unity, depending on the shape of the intersection region. Thus, For anodic reaction (in one electrode compartment):

$$\Delta G^{\ddagger}_{ox} = \Delta G^{\ddagger 0} - \alpha_T F\eta, \tag{2.11}$$

a brief study of the figure as shown in Fig. 2.1, also reveals that at potential E the cathodic reaction (in the same electrode compartment), $\Delta G^{0\ddagger}$ by $(1 - \alpha_T)F\eta$; therefore,

$$\Delta G^{\ddagger}_{red} = \Delta G^{\ddagger 0} + (1 - \alpha_T)F\eta, \tag{2.12}$$

now, let us assume that the rate constants k_f and k_b have an Arrhenius form that can be expressed as

$$k_f = A_f exp[-\Delta G^{\ddagger}_{ox}/RT] \tag{2.13}$$

and

$$k_b = A_b exp[-\Delta G^{\ddagger}_{red}/RT], \tag{2.14}$$

then, inserting the activation energies, Eq. (2.11) and Eq. (2.12), gives

$$k_f = A_f exp[-\Delta G^{\ddagger 0}/RT] exp[\alpha_T f\eta] \tag{2.15}$$

and

$$k_b = A_b exp[-\Delta G^{\ddagger 0}/RT]exp[-(1-\alpha_T)f\eta]. \tag{2.16}$$

Here $f = F/RT$ and $\eta = E - E^0$. The first two factors in each of these expression form a product that is independent of potential and equal to the rate constant at $E = E^0$.

Now consider the special case in which the interface is at equilibrium with a solution in which $C^*_{ox} = C^*_{red}$, in this situation $E = E^0$ and $k_f C^*_{ox} = k_b C^*_{red}$, so that $k_f = k_b$. Thus, E^0 is the potential where the forward and reverse constant have the same value is called the standard rate constant, k^0. The rate constants at other potentials can then be expressed simply in terms of k^0:

$$k_{red} = k^0 exp[-(1-\alpha_T)f\eta] \tag{2.17}$$

and

$$k_{ox} = k^0 exp[\alpha_T f\eta], \tag{2.18}$$

inserting these relations into Eq. (2.8) yields the complete *current-potential characteristics*:

$$i = FAk^0\big[C_{ox}(0,t)e^{\alpha_T f\eta} - C_{red}(0,t)e^{-(1-\alpha_T)f\eta}\big]. \tag{2.19}$$

This relation is very important. It, or a variation derived from it, is used in the treatment of almost every problem requiring an account of heterogeneous kinetics. These results derived from them are known broadly as the *Butler-Volmer* formulation of electrode kinetics [8].

However, in general, the derivation of the electrode potential E from the situation of zero net current, i.e. at E^{eq}, under any experimental conditions is considered. Hence, we have to use the Nernst equation to determine the equilibrium potential E^{eq} for a given composition in the bulk to establish the link between composition in the bulk and equilibrium

$$E^{eq} = E^0 + \frac{RT}{F} ln(\frac{C^*_{ox}}{C^*_{red}}), \tag{2.20}$$

using this relation in Eq. (2.19) and recalling the definition of overpotential, $\eta = E - E^{eq}$, we can rewrite after some rearrangement the Butler-Volmer equation in a different form, as a relation between current and overpotential:

$$i = FAk^0 C_{red}^{*(1-\alpha_T)} C_{ox}^{*\alpha_T} \Big[\frac{C_{red}(0,t)}{C_{red}^*} e^{\alpha_T f\eta} - \frac{C_{ox}(0,t)}{C_{ox}^*} e^{-(1-\alpha_T)f\eta}\Big]. \tag{2.21}$$

Note that, we explicitly distinguish surface concentrations ($C_{red(0,t)}, C_{ox(0,t)}$) from bulk concentrations (C_{red}^*, C_{ox}^*). Bulk concentrations (far away from the interface) determine the equilibrium conditions, surface concentrations, $C_{red/ox(0,t)}$ (at the position of the compact layer), are equal to bulk concentrations, $C_{red/ox}^*$, and no fluxes of species exist. At finite current, surface concentrations will generally be different from bulk concentrations, due to mass transport from the bulk to surface.

In the particular case, when mass transport from the bulk to surface is fast enough (rate of diffusion much larger than rate of reaction), we have $C_{red(0,t)} = C_{red}^*$ and $C_{ox(0,t)} = C_{ox}^*$. In this case, we can write the simplest form of the Butler-Volmer equation (historically the first version),

$$i = i^0 \Big[e^{\alpha_T f\eta} - e^{-(1-\alpha_T)f\eta}\Big]. \tag{2.22}$$

Now, we have three different ways to write the Butler-Volmer equation. You will find all the different forms used throughout electrochemical literature and Eq. (2.22) is the least general form. It can only be used, when all sorts of mass transport limitations can be neglected and the current-potential relation is only determined by the kinetics of charge transfer. Whenever you see people using Eq. (2.22) in a situation with significant mass transport limitations, something is screwed. Moreover Eq. (2.21) can be used for simple electrode structures, when the bulk concentrations are controlled. Eq. (2.20) is the most general form, it explicitly displays all dependencies on concentrations and electrode potential. All other quantities in it are constants.

The transfer coefficient (α_T) is often termed symmetry factor because it determines the dependence of the current density on overpotential [9].

a) If $\alpha_T = 0.5$: The increase in the absolute value of i, $|i|$, is equal for the oxidation as well as for the reduction current($\eta = 0$ and $i = 0$).
b) If $\alpha_T > 0.5$: $|i|$ increases faster for oxidation than for reduction with the same $|\eta|$.
c) If $\alpha_T < 0.5$: $|i|$ increases slower for oxidation than for reduction with the same $|\eta|$.

2.2.2 Basic concepts about the Transfer Coefficient

The actual term "transfer coefficient" suggests that a fraction of the energy is exchanged by the entities involved in electron transfer processes. This idea is acceptable in principle, but in practice the coefficient is often found to have the value of 1/2. It is difficult to see why only half the energy is transferred during an electron transfer in cases where the ions involved are of widely different nature. Attempts to explain or interpret the transfer coefficient can be based on two methods [10].

In the first methods, it is assumed that *in all cases* the transfer coefficient is 1/2 in the elementary process. If this "theoretical" value is contradicted by experience, the phenomenon under study cannot be an elementary electron transfer processes which may be or many not obey Tafel's law. Consequently, the value found experimentally for α must be that of a parameter in the equation governing the total phenomenon under consideration. The final result is an electron transfer, but there is no a *priori* reason why the overall process should obey Tafel's law. In simple cases, such as hydrogen overtension, we can assume that a number of intermediate stages terminate in the final phenomenon. We can make hypothesis on the rates or importance of some of these intermediate steps so as to obtain a law which accounts for the observed results without contradicting Tafel's law. This involves adopting values for α_T which are slightly less or more than the accepted "theoretical" value of 1/2. This explanation of observed overtension processes has been successful in many cases over a limited but fairly wide range of overtensions.

A second method is to begin by establishing a theory of electron transfer reactions from hypotheses which are not closely related to overtension as such. The theoretically obtained relationships can then be used to show whether, and under what conditions, the transfer coefficient is equal to 1/2.

The question of the meaning of the transfer coefficient can be put as follows. If electron transfer phenomena occur in a given system, does the transfer process obey laws which are known and widely confirmed in other branches of physics? If the answer is yes, the transfer coefficient will be at least approximately equal to 1/2, provided that the physical conditions under which the transfer occurs correspond to the approximations which must be made in order to obtain Tafel's law. If, after the approximations have been made, the theoretical and experiment value of α_T is found to be 1/2, it is because the development of the system (at least macroscopically) can be fairly rigorously derived from general laws which were assumed when the theory under consideration was developed. Therefore the problem of the meaning of "α_T" has a mere solution. It is no more than a coefficient which is introduced by various hypothesis and calculations made along the elaboration of the theory. It is so of the same nature that numeric coefficients which appear in other numerous physical or mathematical relations.

There is an alternative possibility. In the most general manner, it is assumed that transfer overtension phenomena must obey Tafel's law. If deviations from this law are found, we assume that a complex reaction is occurring at the electrode and try as far as possible to return to the investigation of elementary processes in the case of a single reaction, in which the transfer coefficient will in fact be 1/2.

2.2.3 Derivation for Transfer Coefficient

The rate constants for oxidation, k_{red}, and reduction, k_{ox}, which is found in Eq. (2.17) and Eq. (2.18) respectively, are important to derive the transfer coefficient. Now let us use these equations in order to get the anodic transfer coefficient as a function the velocity through rate constants and the result is similar to [1]. Using Eq. (2.5) and Eq. (2.6), we can write the forward and backward velocity in the form,

$$\upsilon_f = \upsilon_0 e^{\alpha_A f \eta} \tag{2.23}$$

and

$$\upsilon_b = -\upsilon_0 e^{(\alpha_A - 1) f \eta}, \tag{2.24}$$

where $\upsilon_0 = C_{red} k^0 = C_{ox} k^0$.

But, for this case the overpotential (η) to be very small and have positive value, the two equations, Eq. (2.23) and Eq. (2.24) can be approximately written like,

$$\upsilon_f = \upsilon_0 (1 + \alpha_A f \eta) \tag{2.25}$$

and

$$\upsilon_b = -\upsilon_0 (1 + (\alpha_A - 1) f \eta). \tag{2.26}$$

By rearranging terms one can write the Anodic Transfer Coefficient (α_A) in terms of the forward (υ_f) and backward velocity (υ_b), which is

$$\alpha_A = \frac{\upsilon_f - \upsilon_0}{\upsilon_f + \upsilon_b}. \tag{2.27}$$

In doing so, our α_A is in the range between zero and unity, thus Eq. (2.27) should be written in the form of absolute value

$$\alpha_A = \frac{|\upsilon_f| - |\upsilon_0|}{|\upsilon_f| + |\upsilon_b|}. \tag{2.28}$$

Noting that, the AC is situated at the top of the reaction coordinate either to go to forward or backward, its absolute value of the exchange current is zero based on that the mean value of $|\upsilon_0|$ also zero, thus Eq. (2.28)

$$\alpha_A = \frac{|\upsilon_f|}{|\upsilon_f| + |\upsilon_b|}. \tag{2.29}$$

We would like to mention that Aoki [1] used exactly the same equation as Eq. (2.29) to define ATC (α_A).

2.2.4 The Tafel equation

In the case of a large anodic current density (i) the current as a function of overpotential (η) can be written:

$$lni = lni_0 + \frac{\alpha_A nF\eta}{RT}, \tag{2.30}$$

solving for η gives:

$$\eta = -\frac{2.3RT}{\alpha_A nF} logi_0 + \frac{2.3RT}{\alpha_A nF} logi, \tag{2.31}$$

this corresponds to an early empirical *equation by Tafel* in (1905):

$$\eta = a + b \times logi, \tag{2.32}$$

where "η" is the overpotential, "i" the current density while "a" and "b" are characteristic constants of the electrode system. A plot of electrode potential versus the logarithm of current density is called the "Tafel plot" and the resulting straight line the "Tafel line". "b" is the "Tafel slope" that provides information about the mechanism of the reaction, and "a" provides information about the rate constant of the reaction. Rigorously, the equation should be written as:

$$\eta = a + b \times log\big|i\big|, \tag{2.33}$$

using the absolute value of the current density and the ± sign for anodic and cathodic overpotentials, respectively. Also, the equation holds only for relatively high overpotentials, approximately 0.1 volt or higher.

Chapter 3

Dynamics of an activated complex in an asymmetric potential profile

In the previous Chapter, starting from the basic mechanism of electrode reaction, we derived a simple relation of getting the ATC from the mean forward and backward velocities of the AC. In the present Chapter, we consider the AC as a Browinian particle moving in a potential hill assisted by the thermal kicks and derive relations how to get the Mean Exit Time (MET) for the particle to reach at any one of the end points. The MET will then enable us to find the mean velocities and hence, the expression for the ATC in terms of the potential profile.

3.1 The activated complex in asymmetric potential

Consider a double well potential with the AC placed at the top of the potential hill as shown in Fig. 3.1. The reaction could either go forward and end up in state b or backward and end up in state a. These two end points, a and b, are stable states signifying the reactant and product states, respectively.

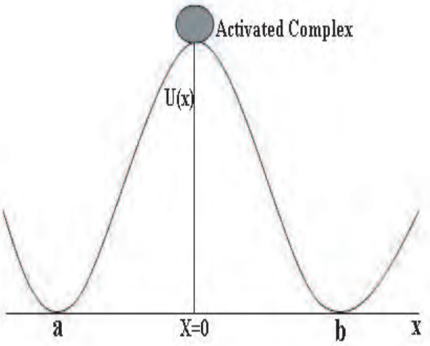

Figure 3.1: Potential profile for the activated complex along a reaction coordinate.

Considering the AC as a Brownian particle, the Langevin equation governing its motion is given by

$$m\frac{d^2x}{dt^2} = -\gamma\frac{dx}{dt} - V'(x) + \sqrt{2k_BT\gamma}\xi(t), \tag{3.1}$$

where x describes the position of the AC at a time t, m is the mass of the AC, γ is the damping (friction) coefficient due to the medium in which the AC is moving, k_B is the Boltzmann's constant, T is the absolute temperature, $V'(x)$ is an external force derivable from possible potential $V(x)$ and the prime denotes differentiation with respect to x, $\xi(t)$ is the Gaussian white noise which is satisfying

$$< \xi(t) >= 0, \tag{3.2}$$

and

$$< \xi(t)\xi(t^{'}) >= \delta(t-t^{'}). \tag{3.3}$$

We consider the AC to be moving under heavy damping (γ very large). Thus the above equation reduces to

$$dx = \frac{-1}{\gamma} V'(x)dt + \sqrt{\frac{2k_BT}{\gamma}} dW(t), \tag{3.4}$$

where $dW(t) = \xi(t)dt$. The Fokker-Planck Equation (FPE) corresponding to this Langevin equation is

$$\partial_t p(x,t) = \frac{1}{\gamma}\partial_x[V'(x)p(x,t)] + \frac{k_BT}{\gamma}\partial_x^2[p(x,t)], \tag{3.5}$$

where $p(x,t)$ is the probability density of finding the AC at position x at time t and γ is taken to be the same through out the medium. For a Langevin equation of the form

$$dx = A(x)dt + B(x)dW(t), \tag{3.6}$$

where $A(x) = -\frac{V'(x)}{\gamma}$ and $B(x) = \frac{2k_BT}{\gamma}$. The forward FPE is given by

$$\partial_t p(x,t) = -\partial_x[A(x)p(x,t)] + \partial_x^2[B(x)p(x,t)], \tag{3.7}$$

while the backward FPE is given by

$$\partial_t p(x,t) = A(x)\partial_x[p(x,t)] + \frac{1}{2}B(x)\partial_x^2[p(x,t)]. \tag{3.8}$$

We begin by calculating the MET taken by the AC to move from the top of the reaction coordinate to go to either the product (oxidation) state or reactant (reduction) state, depending up on the various forces acting on the AC.

3.2 Calculation of mean exit time and anodic transfer coefficient

In this section, we will derive the expression for probability of the MET through a particular end of the interval, MET and mean velocity through both sides and the transfer coefficient i.e. Anodic Transfer Coefficient (ATC). The AC whose dynamics is governed by the FPE, Eq. (3.5), remains in a certain region of x. The solution of these problem can be achieved by using the backward FPE.

3.2.1 Probability of exit time through a particular end of the interval

What is the probability that a particle, initially at x which is located in the interval (a, b), exits through a, and what is its mean exit time? The total probability that the particle exits through a after time t is given by the time integral of the probability current at a [8]. We thus define this probability by

$$\begin{aligned} g_a(x,t) &= -\int_t^{\infty} dt^{'} J(a,t^{'}|x,0) \\ &= -\int_t^{\infty} dt^{'}\{-A(a)p(a,t^{'}|x,0) + \frac{1}{2}\partial_a[B(a)p(a,t^{'}|x,0)]\}. \end{aligned} \tag{3.9}$$

(The negative sign is chosen since we need the current pointing to the left). Similarly, the total probability that the particle exits through b after time t is given by

$$\begin{aligned} g_b(x,t) &= \int_t^{\infty} dt^{'} J(b,t^{'}|,0) \\ &= \int_t^{\infty} dt^{'}\{-A(b)p(b,t^{'}|x,0) + \frac{1}{2}\partial_b[B(b)p(b,t^{'}|x,0)]\}. \end{aligned} \tag{3.10}$$

The probability that (given that it exits through a) it exits after a time t is,

$$Prob(T_a > t) = G_a(x,t) = \frac{g_a(x,t)}{g_a(x,0)}. \tag{3.11}$$

We now find an equation for $g_a(x,t)$. We use the fact that $P(a,t|x,0)$ satisfies a back ward FPE. Noting that

$$A(x)\partial_x g_a(x,t) = -\int_t^{\infty} dt^{'}\{A(x)\partial_x J(a,t^{'}|x,0)\} \tag{3.12}$$

and

$$\frac{B(x)}{2}\partial_x^2 g_a(x,t) = -\int_t^\infty dt^{'}\{\frac{B(x)}{2}\partial_x^2 J(a,t^{'}|x,0)\}, \tag{3.13}$$

while adding these two equations, we get

$$A(x)\partial_x g_a(x,t)+\frac{B(x)}{2}\partial_x^2 g_a(x,t) = -\int_t^\infty dt^{'}\{A(x)\partial_x J(a,t^{'}|x,0)+\frac{B(x)}{2}\partial_x^2 J(a,t^{'}|x,0)\}. \tag{3.14}$$

Thus, $J(a,t^{'}|x,0)$ satisfies the backward FPE, so that we get

$$\begin{aligned} A(x)\partial_x g_a(x,t) + \frac{B(x)}{2}\partial_x^2 g_a(x,t) =& -\int_t^\infty dt^{'}\partial_{t^{'}} J(a,t^{'}|x,0) \\ =& J(a,t|x,0) \\ =& \partial_t g_a(x,t). \end{aligned} \tag{3.15}$$

Note that for the AC, $A(x) = -\frac{V'(x)}{\gamma}$ and $B(x) = \frac{2k_BT}{\gamma}$.

Let $G_a(x,t)$ be the probability that the particle has exited the interval through a any time after t and $P_a(t)dt$ be the probability that has exited through a between t and $t+dt$, i.e.,

$$\begin{aligned} P_a(t)dt =& G_a(x,t) - G_a(x,t+dt), \\ =& -\frac{\partial G_a(x,t)}{\partial t}. \end{aligned} \tag{3.16}$$

Hence, the Mean Exit Time (MET) defined by

$$\begin{aligned} <t>=& \int_0^\infty tP_a(x,t)dt = -\int_0^\infty t\frac{\partial G_a(x,t)}{\partial t}dt, \\ =& \int_0^\infty G_a(x,t)dt. \end{aligned} \tag{3.17}$$

Similarly, the MET through a, $T(a,x)$, is

$$T(a,x) = -\int_0^\infty t\partial_t G_a(x,t)dt = \int_0^\infty G_a(x,t)dt \tag{3.18}$$

and

$$T(a,x)g_a(x,0) = \int_0^\infty g_a(x,t)dt, \tag{3.19}$$

since the system is time homogenous(for $s = -t$), therefore Eq. (3.11) can be rewritten as

$$G_a(x,s) = \frac{g_a(x,s)}{g_a(x,0)}. \tag{3.20}$$

Similarly integrating Eq. (3.15) with respect to t, we get

$$A(x)\partial_x[T(a,x)\Pi_a(x)] + \frac{B(x)}{2}\partial_x^2[T(a,x)\Pi_a(x)] = -\Pi_a(x), \tag{3.21}$$

where we define $\Pi_a(x)$=$g_a(x,0)$ (probability of exit time through a). The boundary condition for Eq. (3.21) follows from those for the backward FPE, namely,

$$\Pi_a(a)T(a,a) = \Pi_a(b)T(a,b) = 0. \tag{3.22}$$

It is clear that, $T(a,a)$ is zero (the time to reach a from a is zero) and $\Pi_a(b)$ is zero (the probability of exiting through a, starting from b, is zero). By letting $t \to 0$ in Eq. (3.15), we see that $J(a,0|x,0)$ must vanish if $a \neq x$, since $p(a,0|x,0) = \delta(x-a)$. Hence, the right hand side of Eq. (3.15) tends to zero and we get,

$$A(x)\partial_x\Pi_a(x) + \frac{B(x)}{2}\partial_x^2\Pi_a(x) = 0, \tag{3.23}$$

the boundary conditions this time is,

$$\begin{aligned} \Pi_a(a) &= 1, \\ \Pi_a(b) &= 0, \end{aligned} \tag{3.24}$$

solving Eq. (3.21) and using this boundary condition, we obtain

$$\Pi_a(x) = \frac{\int_x^b \frac{dy}{\psi(y)}}{\int_a^b \frac{dy}{\psi(y)}}, \tag{3.25}$$

where $\psi(x)$ is an integrating factor which is defined by

$$\psi(x) = exp\{\int_a^x dx^{'}[2A(x^{'})/B(x^{'})]\}. \tag{3.26}$$

In a similar way to find $T(b,x)$ and $\Pi_b(x)$, we start from the probability that exits through b after time t:

$$Prob(T_b > t) = G_b(x,t) = \frac{g_b(x,t)}{g_b(x,0)}, \tag{3.27}$$

lets define $Prob(T_b > t) = G_b(x,t)$ and the equation for $g_b(x,t)$ comes from the $P(b,t|x,0)$ which satisfies the back ward FPE, thus

$$A(x)\partial_x g_b(x,t) + \frac{B(x)}{2}\partial_x^2 g_b(x,t) = J(b,t|x,0) = \partial_t g_b(x,t). \tag{3.28}$$

Therefore, the MET through b, $T(b,0)$, is given by

$$T(b,x) = -\int_0^\infty t\partial_t G_b(x,t)dt = \int_0^\infty G_b(x,t)dt, \tag{3.29}$$

and

$$T(b,x)g_b(x,0) = \int_0^\infty g_b(x,t)dt. \tag{3.30}$$

Similarly integrating Eq. (3.28) with respect to t, we get

$$A(x)\partial_x[T(b,x)\Pi_b(x)] + \frac{B(x)}{2}\partial_x^2[T(b,x)\Pi_b(x)] = -\Pi_b(x), \tag{3.31}$$

where $\Pi_b(x) = g_b(x,0)$ (probability of exits through b). The boundary conditions for Eq. (3.28) follows from those for the back ward FPE namely,

$$\Pi_b(b)T(b,b) = \Pi_b(a)T(b,a). \tag{3.32}$$

Note that, $T(b,b)$ is zero (the time to reach from b to b is zero) and $\Pi_b(a)$ is zero (the probability of exiting through b, starting from a is zero). By letting $t \to 0$ in Eq. (3.28), we see that $J(b,0|x,0)$ must vanish if $b \neq x$, since $P(b,0|x,0) = \delta(b-x)$. Hence, the right hand side tends to zero and we get

$$A(x)\partial_x\Pi_b(x) + \frac{B(x)}{2}\partial_x^2\Pi_b(x) = 0, \tag{3.33}$$

the boundary conditions for Eq. (3.33) is,

$$\begin{aligned} \Pi_b(b) &= 1, \\ \Pi_b(a) &= 0, \end{aligned} \tag{3.34}$$

then by integrating Eq. (3.33) and using this boundary condition, it becomes

$$\Pi_b(x) = \frac{\int_a^x \frac{dy}{\psi(y)}}{\int_a^b \frac{dy}{\psi(y)}}. \tag{3.35}$$

3.2.2 Calculation of mean velocity and transfer coefficient

The mean velocity expressed in terms of the MET through a or b and the distance of the AC moves from the top of the reaction coordinate to go either to the forward (oxidation) state or to the backward (reduction) state. Thus, the mean velocity, $\bar{v}(-x)$, the AC has as it exit through a is given by

$$\bar{v}(-x) = \left|\frac{a}{T(a,x)}\right|, \tag{3.36}$$

similarly the mean velocity, $\bar{v}(x)$, of the AC to exit through b is given by

$$\bar{v}(x) = \left|\frac{b}{T(b,x)}\right|. \tag{3.37}$$

Now we are going to find the expression for $T(a,x)$ and $T(b,x)$. We start from Eq. (3.21) and Eq. (3.31). Let us define that $Y(x) = T(a,x)\Pi_a(x)$, thus Eq. (3.21) can be rewritten as

$$\frac{d^2Y}{dx^2} + \frac{2A(x)}{B(x)}\frac{dY}{dx} = -\frac{2\Pi_a(x)}{B(x)}, \tag{3.38}$$

multiplying both sides by an integrating factor which is defined in Eq. (3.26) we get

$$\frac{d}{dx}(\psi(x)\frac{dY(x)}{dx}) = -\frac{2\Pi_a(x)\psi(x)}{B(x)}, \tag{3.39}$$

Again we define $M(x) = \psi(x)\frac{dY}{dx}$. Then we integrate once Eq. (3.39), with the limit of integration from a to x which is

$$M(x) = M(a) - 2\int_a^x \frac{\Pi_a(y)\psi(y)}{B(y)}dy, \tag{3.40}$$

where $M(a) = \frac{dT}{dx}$ at $x = a$. We know the mean value of Eq. (3.6) is $< dx >= -\frac{V'(x)}{\gamma}dt$, thus $M(a)$ becomes,

$$M(a) = -\frac{\gamma}{V'(a)}, \tag{3.41}$$

finally, after some mathematical steps, Eq. (3.40) can be written as

$$Y(x) = M(a)\int_a^x \frac{dy}{\psi(y)} - 2\int_a^x \frac{dy}{\psi(y)}\int_a^y \frac{\Pi_a(z)\psi(z)}{B(z)}dz. \tag{3.42}$$

Therefore, from the above equation, we obtain the MET through a, $T(a, 0)$, is

$$T(a, x) = \frac{[M(a)\int_a^x \frac{dy}{\psi(y)} - 2\int_a^x \frac{dy}{\psi(y)}\int_a^y \frac{\Pi_a(z)\psi(z)}{B(z)}dz]}{\Pi_a(x)}. \tag{3.43}$$

Similarly we can get the MET through b using the same method. To do that, First we should start from Eq. (3.31) and lets define $Z(x) = T(b, x)\Pi_b(x)$. In all cases the variables x,y and z are dummy variables. Thus the solution to Eq. (3.31) can be written as

$$Z(x) = -\left[N(b)\int_x^b \frac{dy}{\psi(y)} + 2\int_x^b \frac{dy}{\psi(y)}\int_y^b \frac{\Pi_b(z)\psi(z)}{B(z)}dz\right], \tag{3.44}$$

finally the expression for MET through b, $T(b, 0)$, is

$$T(b, x) = -\frac{N(b)\int_x^b \frac{dy}{\psi(y)} + 2\int_x^b \frac{dy}{\psi(y)}\int_y^b \frac{\Pi_b(z)\psi(z)}{B(z)}dz}{\Pi_b(x)}, \tag{3.45}$$

where $N(b) = \frac{-\gamma}{V'(b)}$. From the above expressions, we can also get the ATC, α_A, this is derived in Chapter 2 and Eq. (2.29) can be rewritten as,

$$\alpha_A = \frac{\bar{\upsilon}(x)}{\bar{\upsilon}(x) + \bar{\upsilon}(-x)}, \tag{3.46}$$

by substituting Eqs. (3.35) and (3.36) in Eq. (3.46), we get

$$\alpha_A = \frac{1}{1 + \left|\frac{aT(b,x)}{bT(a,x)}\right|}, \tag{3.47}$$

for the case of model barrier potentials. When the AC is situated at the origin, the ATC (α_A) becomes

$$\alpha_A = \frac{1}{1 + \left|\frac{aT(b,0)}{bT(a,0)}\right|}. \tag{3.48}$$

Chapter 4

Determination of the mean exit time and anodic transfer coefficient for model potentials

In the previous Chapter, we presented a method for the determination of the MET for a general potential hill. In this Chapter, we will explicitly derive the expression for MET and then ATC for three particular model potential hills. The AC is initially situated at the top of the reaction coordinate. The three model potential profiles are illustrated below in Figs. 4.1, 4.2 and 4.3. While the AC is free to diffuse along the potential profile, it may go either to the forward (oxidation) or backward (reduction) state.

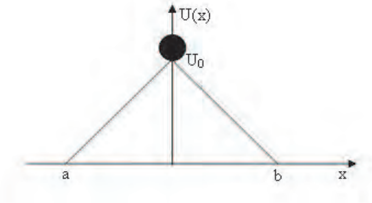

Figure 4.1: Plot of two linearly connected potential hill with the activated complex placed at the top of the reaction coordinate.

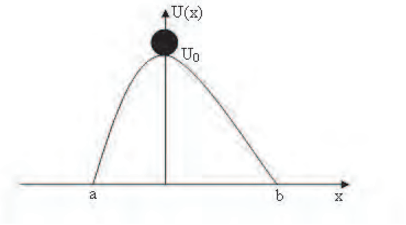

Figure 4.2: Plot of an inverted parabolic potential hill with the activated complex placed at the top of the reaction coordinate.

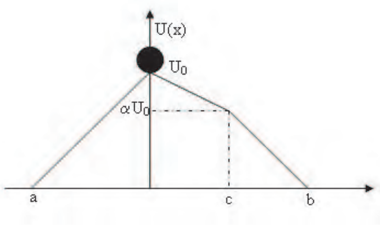

Figure 4.3: Plot of three linearly connected potential hill with the activated complex placed at the top of the reaction coordinate.

Now we will define the equation describing the model potential hills. The first model potential (fmp) profile of Fig. 4.1 is described by

$$V_1(x) = \begin{cases} U_0(-\frac{x}{a}+1) & \text{if } a \le x \le 0 \ , \\ U_0(-\frac{x}{b}+1) & \text{if } 0 \le x \le b \ . \end{cases} \tag{4.1}$$

The second model potential (smp) profile of Fig. 4.2 is denoted by

$$V_2(x) = \begin{cases} U_0(-\frac{x^2}{a^2}+1) & \text{if } a \le x \le 0 \ , \\ U_0(-\frac{x^2}{b^2}+1) & \text{if } 0 \le x \le b \ . \end{cases} \tag{4.2}$$

Lastly, the third model potential (tmp) profile of Fig. 4.3 is presented by

$$V_3(x) = \begin{cases} U_0(-\frac{x}{a}+1) & \text{if } a \le x \le 0 \ , \\ U_0(-\frac{(1-\alpha)}{c}x+1) & \text{if } 0 \le x \le c \ , \\ U_0\alpha(\frac{b-x}{b-c}) & \text{if } c \le x \le b \ . \end{cases} \tag{4.3}$$

Thus, by using these model potentials of Eq. (4.1), Eq. (4.2) and Eq. (4.3), we can calculate the MET and ATC corresponding to each model potential.

4.1 Mean exit time from $x = 0$ to $x = a$ and from $x = 0$ to $x = b$ for first model potential

The AC is considered to be initially placed at $x = 0$. Therefore to find the MET through a, $T(a, 0)$ using Eq. (3.43) and then start the derivation of $T(a, 0)$ for fmp as shown in Fig. 4.1, to be

$$T(a,0) = \frac{M_1(a) \int_a^0 \frac{dy}{\psi_1(y)} - 2 \int_a^0 \frac{dy}{\psi_1(y)} \int_a^y \frac{\Pi_a(z)\psi_1(z)}{B(z)} dz}{\Pi_a(0)}, \tag{4.4}$$

where $M_1(a) = \frac{a}{Dk}$, $k = \frac{U_0}{\gamma D}$ and $D = \frac{k_B T}{\gamma}$ and $\psi_1(x)$ can be written as

$$\psi_1(x) = \begin{cases} \psi_{11}(x) = \frac{1}{d} e^{\frac{kx}{a}} & \text{if } a \leq x \leq 0 \ , \\ \psi_{12}(x) = \frac{1}{d} e^{\frac{kx}{b}} & \text{if } 0 \leq x \leq b \ , \end{cases} \tag{4.5}$$

where $d = e^k$. By applying this equation to $\Pi_a(x)$ which is found in Eq. (3.25) is,

$$\Pi_a(x) = \frac{\int_x^0 \frac{dx'}{\psi_{11}(x')} + \int_0^b \frac{dx'}{\psi_{12}(x')}}{\int_a^0 \frac{dx'}{\psi_{11}(x')} + \int_0^b \frac{dx'}{\psi_{12}(x')}}, \tag{4.6}$$

then substituting Eq. (4.5) in Eq. (4.6), Eq. (4.6) becomes

$$\Pi_a(x) = \frac{a(1 - e^{\frac{-kx}{a}}) + b(e^{-k} - 1)}{(a - b)(1 - e^{-k})}. \tag{4.7}$$

Taking $x = 0$ in Eq. (4.7) will be

$$\Pi_a(0) = \frac{b}{b - a}. \tag{4.8}$$

Finally substituting Eqs. (4.7) and (4.8) to Eq. (4.4), we get the expression for the MET through a, $T(a, 0)$, as

$$T(a,0) = \frac{a^2}{Dk} \left[-\left(\frac{2b - a}{b}\right) \left(\frac{e^k - 1}{k}\right) - \frac{2a}{b} \left(\frac{1}{1 - e^{-k}}\right) + \frac{a}{bk} \left(\frac{e^k - e^{-k}}{1 - e^{-k}}\right) + 1 \right], \tag{4.9}$$

similarly to find the MET through b, $T(b,0)$, lets start from Eq. (3.45) which can be rewritten as

$$T(b,0) = -\frac{N_1(b)\int_0^b \frac{dy}{\psi_1(y)} + \frac{1}{D}\int_0^b \frac{dy}{\psi_1(y)}\int_y^b \Pi_b(z)\psi_1(z)dz}{\Pi_b(0)}, \tag{4.10}$$

where $N_1(b) = \frac{b}{Dk}$. On the other hand Eq. (3.35) for this model can be written as

$$\Pi_b(x) = \frac{\int_a^0 \frac{dx'}{\psi_{11}(x')} + \int_0^x \frac{dx'}{\psi_{12}(x')}}{\int_a^0 \frac{dx'}{\psi_{11}(x')} + \int_0^b \frac{dx'}{\psi_{12}(x')}}. \tag{4.11}$$

Substituting Eq. (4.5) in Eq. (4.11), we obtain

$$\Pi_b(x) = \frac{a(1-e^{-k}) + b(-1+e^{\frac{-kx}{b}})}{(a-b)(1-e^{-k})}. \tag{4.12}$$

Fixing at $x = 0$, one can rewrites Eq. (4.12) as

$$\Pi_b(0) = \frac{a}{a-b}. \tag{4.13}$$

Using the expression Eqs. (4.12) and (4.13) in Eq. (4.10), we find that the expression for the MET through b, $T(b,0)$, as

$$T(b,0) = \frac{b^2}{Dk}\left[-\left(\frac{2a-b}{a}\right)\left(\frac{e^k-1}{k}\right) - \frac{2b}{a}\left(\frac{1}{1-e^{-k}}\right) + \frac{b}{ak}\left(\frac{e^k-e^{-k}}{1-e^{-k}}\right) + 1\right]. \tag{4.14}$$

Note that, using Eqs. (4.9) and (4.14) can also find the ATC for the AC in this model potential profile.

4.2 Mean exit time from $x = 0$ to $x = a$ and from $x = 0$ to $x = b$ for second model potential

Consider the situation as shown in Fig. 4.2 and thus the MET though a, $T(a,0)$, can be obtained from Eq. (3.43) which is rewritten as

$$T(a,0) = \frac{M_2(a)\int_a^0 \frac{dy}{\psi_2(y)} - 2\int_a^0 \frac{dy}{\psi_2(y)}\int_a^y \frac{\Pi_a(z)\psi_2(z)}{B(z)}dz}{\Pi_a(0)}, \tag{4.15}$$

where $M_2(a) = \frac{a}{2Dk}$. The integrating factor for smp, $\psi_2(x)$, is written as,

$$\psi_2(x) = \begin{cases} \psi_{21}(x) = \frac{1}{d} e^{\frac{kx^2}{a^2}} & \text{if } a \leq x \leq 0 \ , \\ \psi_{22}(x) = \frac{1}{d} e^{\frac{kx^2}{b^2}} & \text{if } 0 \leq x \leq b \ . \end{cases} \tag{4.16}$$

From the above equation, the expression for Eq. (3.25) one can attain

$$\Pi_a(x) = \frac{\int_x^0 \frac{dx^{'}}{\psi_{21}(x^{'})} + \int_0^b \frac{dx^{'}}{\psi_{22}(x^{'})}}{\int_a^0 \frac{dx^{'}}{\psi_{21}(x^{'})}, + \int_0^b \frac{dx^{'}}{\psi_{22}(x^{'})}}. \tag{4.17}$$

At $x = 0$, we can write Eq. (4.17) in a simple form:

$$\Pi_a(0) = \frac{\int_0^b \frac{dx^{'}}{\psi_{22}(x^{'})}}{\int_a^0 \frac{dx^{'}}{\psi_{21}(x^{'})} + \int_0^b \frac{dx^{'}}{\psi_{22}(x^{'})}}. \tag{4.18}$$

The above expressions cannot be solved analytically. Instead we use numerical method to evaluate the integral. Thus by plugging Eq. (4.17) and Eq. (4.18) to Eq. (4.15), we can get the value for MET through a, $T(a, 0)$. Similarly the value of MET through b, $T(b, 0)$ also cannot be solved analytically, therefore we use the numerical method and Eq. (3.45) at $x = 0$ can be rewritten as

$$T(b, 0) = -\frac{N_2(b) \int_0^b \frac{dy}{\psi_2(y)} + \frac{1}{D} \int_0^b \frac{dy}{\psi_2(y)} \int_y^b \Pi_b(z) \psi_2(z) dz}{\Pi_b(0)}, \tag{4.19}$$

where $N_2 = \frac{b}{2Dk}$. The expression of Eq. (3.35) for smp can be rewritten as

$$\Pi_b(x) = \frac{\int_a^0 \frac{dx^{'}}{\psi_{21}(x^{'})} + \int_0^x \frac{dx^{'}}{\psi_{22}(x^{'})}}{\int_a^0 \frac{dx^{'}}{\psi_{21}(x^{'})} + \int_0^b \frac{dx^{'}}{\psi_{22}(x^{'})}}. \tag{4.20}$$

Fixing $x = 0$, we get

$$\Pi_b(0) = \frac{\int_a^0 \frac{dx^{'}}{\psi_{21}(x^{'})}}{\int_a^0 \frac{dx^{'}}{\psi_{21}(x^{'})} + \int_0^b \frac{dx^{'}}{\psi_{22}(x^{'})}}. \tag{4.21}$$

Finally by plugging Eqs. (4.20) and (4.21) in Eq. (4.19), we obtain the MET that exits through b numerically. Using Eqs. (4.15)and (4.19), we can also find the ATC for the smp.

4.3 Mean exit time from $x = 0$ to $x = a$ and from $x = 0$ to $x = b$ for third model potential

Now let use consider the potential profile as shown in Fig. 4.3. Then the expression for MET through a, $T(a, 0)$ which is found in Eq. (3.43) can be expressed as

$$T(a,0) = \frac{M_3(a)\int_a^0 \frac{dy}{\psi_3(y)} - 2\int_a^0 \frac{dy}{\psi_3(y)}\int_a^y \frac{\Pi_a(z)\psi_3(z)}{B(z)}dz}{\Pi_a(0)}, \tag{4.22}$$

where $M_3(a) = \frac{a}{Dk}$ and $B(z) = 2D$.

The expression for $\psi_3(x)$ can be written as

$$\psi_3(x) = \begin{cases} \psi_{31} = \frac{1}{d}e^{\frac{kx}{a}} & \text{if } a \le x \le 0\ , \\ \psi_{32} = \frac{1}{d}e^{\frac{k(1-\alpha)x}{c}} & \text{if } 0 \le x \le c\ , \\ \psi_{33} = \frac{1}{d^{\frac{\alpha b}{b-c}}}e^{\frac{k\alpha x}{b-c}} & \text{if } c \le x \le b\ . \end{cases} \tag{4.23}$$

From the above equation, Eq. (3.25) can be rewritten as

$$\Pi_a(x) = \frac{\int_x^0 \frac{dx'}{\psi_{31}(x')} + \int_0^c \frac{dx'}{\psi_{32}(x')} + \int_0^b \frac{dx'}{\psi_{33}(x')}}{\int_a^0 \frac{dx'}{\psi_{31}(x')} + \int_0^c \frac{dx'}{\psi_{32}(x')} + \int_0^b \frac{dx'}{\psi_{33}(x')}}. \tag{4.24}$$

Then, we substitute Eq. (4.23) in Eq. (4.24) becomes

$$\Pi_a(x) = \frac{B' + a(1 - e^{\frac{-kx}{a}})}{A'}. \tag{4.25}$$

Fixing $x = 0$, we get

$$\Pi_a(0) = \frac{B'}{A'}, \tag{4.26}$$

where $A' = a(1 - e^{-k}) + B'$ and $B' = \frac{c}{1-\alpha}(-1 + e^{-k(1-\alpha)}) + \frac{(b-c)}{\alpha e^k}(1 - e^{k\alpha})$.

Finally substituting Eqs. (4.25) and (4.26) in Eq. (4.22), we find that the expression for the MET through a, $T(a, 0)$, to be

$$T(a,0) = -\frac{a^2}{Dk}\left[\frac{A'}{B'}\left(\frac{e^k - 1}{k}\right) - 1 + \frac{e^k - 1}{k} + \frac{a}{B'}\left(-2 + \frac{e^k - e^{-k}}{k}\right)\right], \tag{4.27}$$

Similarly to find the MET through b, $T(b,0)$, which is found in Eq. (3.45) at $x=0$ can be rewritten as

$$T(b,0) = -\frac{N_3(b)\int_0^b \frac{dy}{\psi_3(y)} + \frac{1}{D}\int_0^b \frac{dy}{\psi_3(y)}\int_y^b \Pi_b(z)\psi_3(z)dz}{\Pi_b(0)}, \tag{4.28}$$

where $N_3(b) = \frac{b-c}{k\alpha}$ and by substitution Eq. (4.23) in Eq. (4.28), it becomes

$$T(b,0) = -\frac{N_3(b)\int_0^c \frac{dy}{\psi_{32}(y)} + \int_c^b \frac{dy}{\psi_{33}(y)} + \frac{1}{D}\left[\int_0^c \frac{dy}{\psi_{32}(y)}\int_y^c \Pi_b^1(z)\psi_{32}(z)dz + Tb\right]}{\Pi_b(0)}, \tag{4.29}$$

where $Tb = \int_0^c \frac{dy}{\psi_{32}(y)}\int_c^b \Pi_b^2(z)\psi_{33}(z)dz + \int_c^b \frac{dy}{\psi_{33}(y)}\int_y^b \Pi_b^3(z)\psi_{33}(z)dz.$
We define $\Pi_b^1(z)$, $\Pi_b^2(z)$ and $\Pi_b^3(z)$ in this way

$$\Pi_b^1(z) = \frac{\int_a^0 \frac{dy}{\psi_{31}(y)} + \int_0^z \frac{dy}{\psi_{32}(y)}}{\int_a^0 \frac{dy}{\psi_{31}(y)} + \int_0^c \frac{dy}{\psi_{32}(y)} + \int_c^b \frac{dy}{\psi_{33}(y)}} \tag{4.30}$$

and

$$\Pi_b^2(z) = \frac{\int_a^0 \frac{dy}{\psi_{31}(y)} + \int_0^c \frac{dy}{\psi_{32}(y)} + \int_c^z \frac{dy}{\psi_{33}(y)}}{\int_a^0 \frac{dy}{\psi_{31}(y)} + \int_0^c \frac{dy}{\psi_{32}(y)} + \int_c^b \frac{dy}{\psi_{33}(y)}}. \tag{4.31}$$

But $\Pi_b^2(z) = \Pi_b^3(z)$. Then by plugging Eq. (4.23) in Eq. (4.29). We found that

$$\Pi_b^1(z) = \frac{1}{A'}\left[a(1-e^{-k}) + \frac{c}{1-\alpha}(e^{\frac{-kz(1-\alpha)}{c}} - 1)\right] \tag{4.32}$$

and

$$\Pi_b^2(z) = \Pi_b^3(z) = \frac{1}{A'}\left[a(1-e^{-k}) + \frac{c}{1-\alpha}(e^{\frac{-k(1-\alpha)}{c}} - 1) + \frac{b-c}{\alpha e^k}[e^{\frac{\alpha k(b-z)}{b-c}} - e^{\alpha k}]\right]. \tag{4.33}$$

Finally we get the expression of MET through b, $T(b,0)$, is

$$T(b,0) = \frac{A'}{D(B'-A')}\left\{TB + \frac{b-c}{\alpha k^2}\left[\frac{c}{1-\alpha}(e^k - e^{-\alpha k}) + (\frac{b-c}{\alpha})(e^k - 1)\right]\right\}. \tag{4.34}$$

Where the expression for TB is given in Appendix A Eq. (A.1). Thus using Eqs. (4.27) and (4.34), we can find the ATC for the AC.

4.4 Result and Discussion

In this section, the expression for the MET through a, $T(a, 0)$, the MET through b, $T(b, 0)$, and the ATC are written in terms of a, b, U_0, α and T. By plugging the values to the expression for the MET and ATC, we can easily obtain the results for the MET and ATC. To do this, we will fix a and vary one of the values of either U_0, b and α. Thus, by imposing the expressions of MET to ATC, we will obtain the values of ATC ranging from 0.5 up to an extraordinarily small value of 0.1 and these results will be discussed for the MET and ATC both numerically and analytically under a particular model potential profiles. Moreover the numerical results have some error but the errors come from machine errors so we didn't consider it for our results. For all model potential profiles, the given temperature is room temperature ($T = 300K$).

4.4.1 Analytical and Numerical results for first model potential

In the fmp, we find the MET through a, $T(a, 0)$ and b, $T(b, 0)$, we get both the analytical and numerical results which are almost equal and the ATC can be found from the MET result. Moreover the MET through a become smaller and smaller while we changed the b value but we fixed the value of a, the decrease in MET comes from asymmetric in barrier potential. We now study the effect analytically and numerically and we plotted $T(a, 0)$, as a function of b for various values of the barrier height U_0. The plots of $T(a, 0)$ versus b both analytically and numerically are shown in Figs. 4.4 and 4.5, respectively, for $a = -1$, $U_0 = 1k_BT, 2k_BT$ and $4k_BT$.

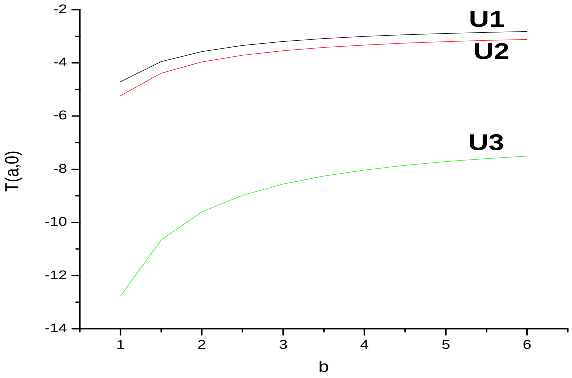

Figure 4.4: Plot of $T(a,0)$ versus b analytically for some U_0(U1= $1k_BT$, U2= $2k_BT$ and U3= $4k_BT$).

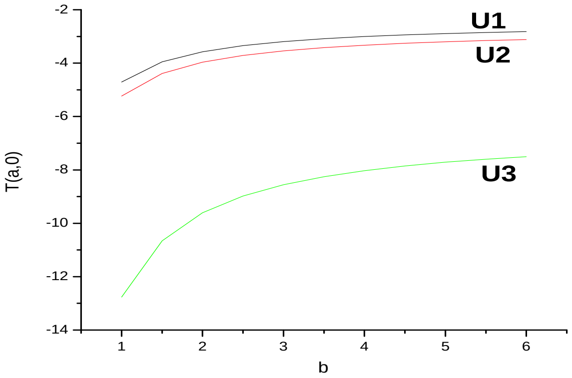

Figure 4.5: Plot of $T(a,0)$ versus b numerically for some U_0(U1= $1k_BT$, U2= $2k_BT$ and U3= $4k_BT$).

The MET through b increases as we vary the b value for fixed value of a. This is due to highly asymmetric in the barrier potential. We now study the effect analytically and numerically and plotted $T(b,0)$, as a function of b for various values of the barrier height U_0. The plots of $T(a,0)$ versus b both analytically and numerically are shown in Figs. 4.6 and 4.7, respectively, for $a=-1$, $U_0=1k_BT, 2k_BT$ and $4k_BT$.

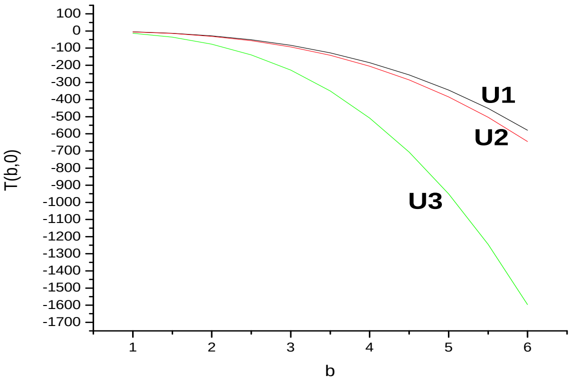

Figure 4.6: Plot of $T(b,0)$ versus b analytically for some U_0(U1= $1k_BT$, U2= $2k_BT$ and U3= $4k_BT$).

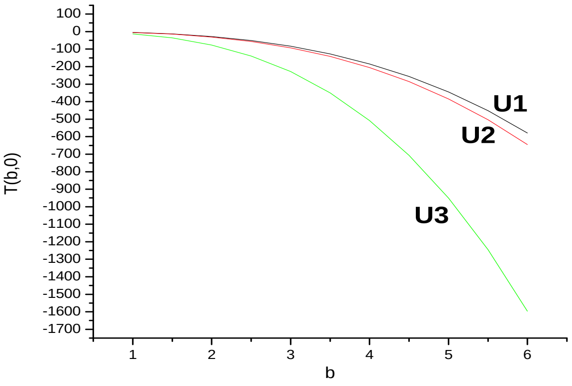

Figure 4.7: Plot of $T(b,0)$ versus b numerically for some U_0(U1= $1k_BT$, U2= $2k_BT$ and U3= $4k_BT$).

We begin from the symmetric potential profile with ($|a| = |b|$), i.e. initially we have the same MET through a and b, during this time the ATC becomes similar with the conventional value of ($\alpha_A = 0.5$) and it then decreases until it reaches to an extraordinarily value of ($\alpha_A \approx 0.1$). The plots of α_A versus b both analytically and numerically are shown in Figs. 4.8 and 4.9 below respectively for $a = -1$, $U_0 = 1k_BT, 2k_BT$ and $4k_BT$.

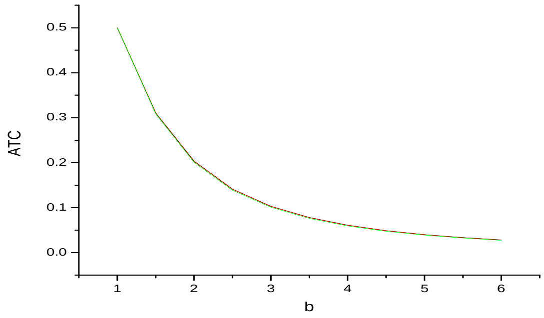

Figure 4.8: Plot of anodic transfer coefficient versus b analytically for some U_0=$1k_BT, 2k_BT$ and $4k_BT$ but the graphs overlapped on each other.

The plots of Figs. 4.4 and 4.5, show us that $T(a, 0)$ keep decreasing but $T(b, 0)$ increases as we increase the value of b. Similarly as we increase the barrier height U_0, both $T(a, 0)$ and $T(b, 0)$, become increase. The increment in barrier height to a very large values has nothing to do with ATC as shown in Fig. 4.8 and Fig. 4.9. Moreover, from the plot of ATC versus b, we find that, the ATC takes a maximum value at $\alpha_A = 0.5$ and then decreases as we increase the b value.

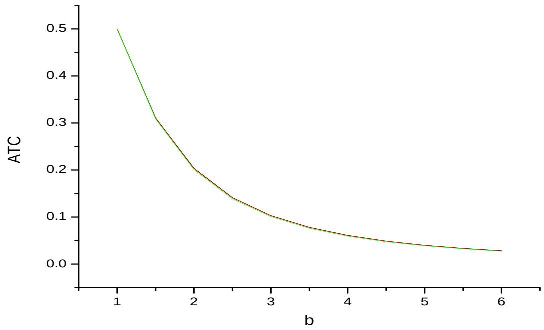

Figure 4.9: Plot of anodic transfer coefficient versus b numerically for some $U_0 = 1k_BT, 2k_BT$ and $4k_BT$ but the graphs overlapped on each other.

4.4.2 Numerical results for second model potential

For smp model profile, we can not calculate analytically the MET that exits through a and b. Rather we calculate it using numerical method and we get some results. Using this result we can get the ATC. Overall we get similar results with the FMP. Now we will study the effect of numerical results. We plotted $T(a,0), T(b,0)$ and α_A as a function of b for various values of b and U_0. We begin from the symmetric potential at $(|a| = |b|)$, i.e. initially we have the same MET that exits through a and b. Thus, for the ATC, we get similar result to the fmp. The plot of $T(a,0)$ versus b, $T(b,0)$ versus b and α_A versus b are shown in Figs. 4.10, 4.11 and 4.12, respectively, for $a = -1$, $U_0 = 1k_BT, 2k_BT$ and $4k_BT$.

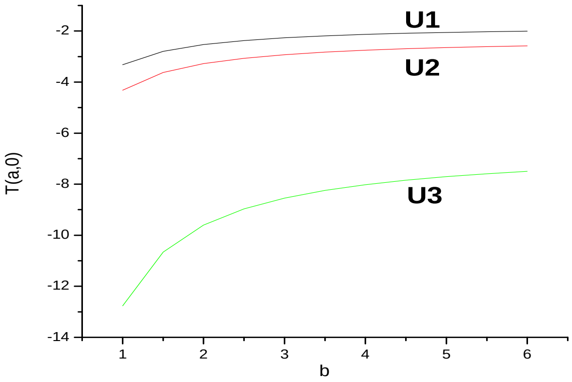

Figure 4.10: Plot of $T(a,0)$ versus b for some U_0(U1$=1k_BT$, U2$=2k_BT$ and U3$=4k_BT$).

The plots for smp show similar property with that of fmp as we increase the b value. Moreover, $T(a,0)$ and α_A show decreasing but $T(b,0)$ shows increasing as we increase the value of b. Similarly the increment in barrier height potential has nothing to do with the result of ATC, this is shown in Fig. 4.12 and the ATC starts from the value of ($\alpha_A = 0.5$) i.e.(a conventional value for simple electrochemical reaction), up to very small value of ($\alpha_A \approx 0.1$).

4.4.3 Analytical result for third model potential

The tmp barrier potential model, as shown in Fig. 4.3, shows similar profile with that of the real model as shown in Fig. 1.2. Therefore, for this model we can verify that the MET through a ($T(a,0)$) and b ($T(b,0)$) as well as ATC can be obtained analytically. To do this, lets find their slopes from Fig. 4.3, which is obtained in Eq. (4.3). Thus, the three slopes s_1, s_2 and s_3 are defined by

$$S = \begin{cases} s_1 = -\frac{U_0}{a} & \text{if } a \le x \le 0 \ , \\ s_2 = \frac{U_0(\alpha-1)}{c} & \text{if } 0 \le x \le c \ , \\ s_3 = \frac{\alpha U_0}{c-b} & \text{if } c \le x \le b \ , \end{cases} \tag{4.35}$$

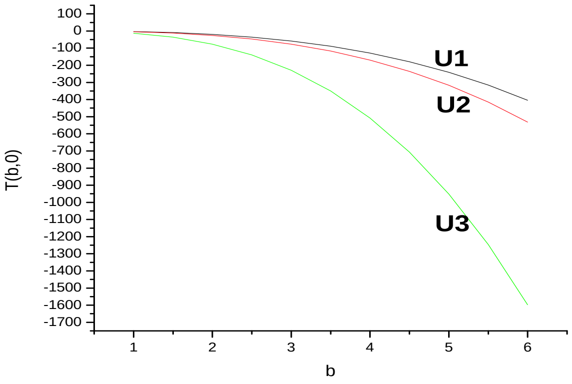

Figure 4.11: Plot of $T(b,0)$ versus b for some U_0(U1= $1k_BT$, U2= $2k_BT$ and U3= $4k_BT$).

where α is a constant value ranges from 0.75 up to 0.95 therefore, to obtain appropriate results for $T(a,0)$, $T(b,0)$ and ATC, the slopes should be arranged as,

$$|s_2| \leq |s_3| \leq |s_1|. \tag{4.36}$$

Applying the above condition, we plotted the ATC (α_A) versus α for $a = -1.0$, $b = 2.0$, $c = 0.25$ and $U_0 = 15k_BT$.

This graph is similar to the previous model graphs. Thus, the ATC becomes small while we increase the value of α and it starts decreasing from the value of 0.35 and reaches less than 0.1 value. But the small value we have got for ATC is similar to [1], in which the small value comes from the asymmetry of the tmp profile. The reason we took for barrier height $U_0 = 15k_BT$ is most of the time experiments taking above $U_0 = 10k_BT$ to conduct the experiment of electrochemical reaction.

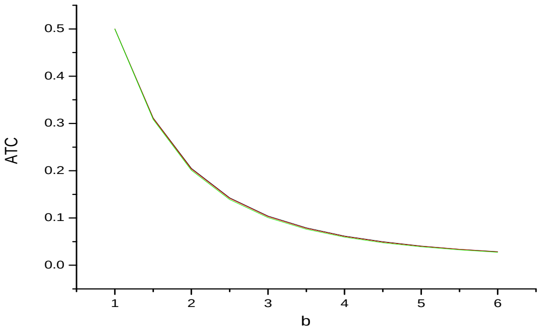

Figure 4.12: Plot of anodic transfer coefficient versus b for $U_0 = 1k_BT, 2k_BT$ and $4k_BT$ but the graphs overlapped on each other.

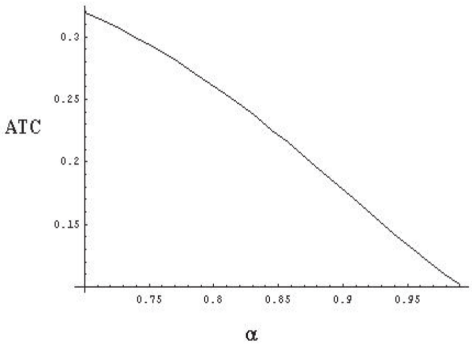

Figure 4.13: Plot of anodic transfer coefficient versus α for $U_0 = 15k_BT$.

Chapter 5

Summary and Conclusion

We considered three model potential hills and find expressions for their ATC. The AC is initially located at the barrier top of the reaction coordinate and allowed to move either forward or backward under the thermal kick, it gets from the background. Since the diffusion of the AC is dependent on the potential profile. It arrives at either the reactant or the product side with different values of MET under asymmetric barrier potential. Based on this, we find that for model potential barrier, the MET through a and b as well as the ATC. Thus we have explored the asymmetric potential profile which gives the values of the ATC ranging from 0.5 to as low as 0.1, this can be done by varying both the reaction coordinate points and the barrier heights. In general, the transfer coefficient often termed as symmetry factor through model barrier potentials and its value is very essential for various electrochemical reaction.

In conclusion, we believe that our work has, for the first time, quantitatively explored the quantities that determine the magnitude of the ATC through MET method. Therefore, our methods of getting the ATC is different from that used by Aoki [1]. As such, it would be interesting to compare Aoki's result with that found using our methods. This part is yet to be investigated.

Appendix A

Appendix

In this Appendix, we give explicitly the expression for the constants of MET through b, $T(b,0)$ for tmp, which is found in Eq.(4.34). The constant TB can be rewritten as

$$TB = TB1 + TB2 + TB3, \tag{A.1}$$

where $TB1, TB2$ and $TB3$ is given by

$$TB1 = \frac{c^2}{A'k(1-\alpha)}\left[\frac{2c}{1-\alpha} + \frac{c}{k(1-\alpha)^2}\left(e^{-k(1-\alpha)} - e^{k(1-\alpha)}\right) + a(1-e^{-k})\left(-1 + \frac{e^k - 1}{k(1-\alpha)}\right)\right], \tag{A.2}$$

$$TB2 = \frac{c(b-c)}{A'\alpha k(1-\alpha)}\left(e^k - e^{\alpha k}\right)\left[\frac{b-c}{e^k} + \frac{1}{k}\left(A' - (\frac{b-c}{\alpha e^k})\right)(1-e^{-\alpha k})\right] \tag{A.3}$$

and

$$TB3 = \frac{(b-c)^2}{\alpha A'k}\left[-A'\left(1 + \frac{1-e^{\alpha k}}{\alpha k}\right) + \frac{b-c}{\alpha e^k}\left(1 + e^{\alpha k} + \frac{2(1-e^{\alpha k})}{\alpha k}\right)\right]. \tag{A.4}$$

Bibliography

[1] K. Aoki, J. Electroanal. Chem. **569** (2004) 121-125.

[2] K. Aoki, Kawase, J. Electroanal. Chem. **377** (1994) 125.

[3] K. Aoki, T. Aramoto, Y. Hoshino, J. Electroanal. Chem. **340** (1992) 127.

[4] Y. Tezuka, K. Aoki, J. Electroanal. Chem. **273** (1989) 161.

[5] Y. Tezuka, K. Aoki, T. Ishii, Electrochim. Acta **44** (1999) 1871.

[6] A. J. Bard, L. R. Faulkner, Electrochemical Methods; Fundamentals and Applications, Wiley, New York, 2001, P.115-130.

[7] C. W. Gardiner, Handbook of Stochastic Methods for Physics, Chemistry and Natural Sciences, Second Edition, Springer, New York, 1985.

[8] Christopher M. A., Brett, Electrochemistry; Principles, Methods and Application, Oxford; New York, Oxford Univeristy Press, 1993.

[9] http://www.Chem 465/865/lecture 14-16/2004.

[10] J. P. Brenet, K. Traore, Transfer Coefficients in Electrochemical kinetics, Academic Press Inc., New York, 1971.

DECLARATION

I hereby declare that this thesis is my original work and has not been presented for a degree in any other University. All sources of material used for the thesis have been duly acknowledged.

Name: ***Dawit Solomon***

Signature:_______________

This thesis has been submitted for examination with my approval as university advisor.

Name: ***Dr. Mulugeta Bekele***

Signature:_______________

Addis Ababa University

Department of Physics

June, 2006.