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Thin-layer cyclic voltammetric studies electron transfer across liquid/liquid interface

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ABSTRACT

Thin layer cycle voltammetry is one of the most efficient methods to investigate liquid/liquid interface. The advantages of this approach lie on its simplicity and effectiveness. The paper represents the progress that has been made in experiments and theories, analyzing the factors that affect rate constants and discussing how to get steady-state currents.

1. Introduction

Since the first experiment on liquid/liquid interface began with Nernst in 1902 [1] who took the lead in studying electric current phenomenon of NB/H_2O interface (NB: Nitrobenzene), considerable achievements have been made not only in the experiments but in theories about charge transformation between the two immiscible electrolyte solutions [2-6]. The study of electron transfer through liquid/liquid interface has attracted great attention because of the importance of liquid/liquid interface, which are widely used in many fields, such as ion-selective sensor, phase transfer catalysis, pharmacology, colloidal chemistry, and solar energy transformation, as well as imitation biomembrane [7-8]. Liquid/liquid interface, which has another way of saying oil/water interface; "Interface between two immiscible electrolyte solutions (ITIES)". ITIES is a new frontier branch of electrochemistry and electro analytical chemistry between classical electrochemistry and chemical sensor. ITIES is used to study some electrochemical processes within the thin layers when charges transfer at adjacent immiscible liquid/liquid interface. The charge transformation reaction can be classified into three main categories: Ion transfer (IT), Electron transfer (ET) and Assisted ion transfer (AIT) [9]. Frequently, IT or ET is mainly studied on the liquid/liquid interface and in contrast to ET, IT is a little easier to study at the liquid/liquid interface. In general, there are two conditions must be met to study ET between liquid/liquid interface. First, potential in the organic phase has to match the potential of electro active substances in the aqueous phase. Secondly, the ions of hydrophobic organic solvents trapped at the electrode are not allowed to cross the liquid/liquid interface as the electrical transfer from organic phase to aqueous phase, thus, the study of electron transfer is not easy.

It is difficult to find the appropriated systems for potential of redox-active specimen within the organic phases. Compared ET with IT, ET lags behind IT and there is just a little dynamic data obtained in the course of the ITIES' development. Main methods used to study liquid/liquid interface are : Micro-tube Technique; Spectral Electrochemical; Micro-drop; Electrochemical methods; Scanning Electrochemical Microscopy (SEM); Thin-layer Cyclic Voltammetry (TLCV); Second Harmonic Generation (SHG) and Computer Modeling [10] and so on. Among them the TLCV is introduced in this paper. The advantages of this approach lie on its simplicity and without complexities in its manipulation. The cost is inexpensive and economical and the quantity of its usage is only mL. [11]. Due to the extraction function to trace elements, TLCV is an efficient method to detect the uneasy dissolved compounds, inactive metals or rare low yield metals. Electro active substances in TLCV have relative wider and more expansive potential window value than they have in water.

It was Samec [12] who applied four-electrode constant potency in TLCV to study electron transfer through liquid/liquid interface and published the first article about it. Schiffrin and Girault [13-18] have contributed substantially to the understanding of electron transfer kinetics at liquid/liquid interface on the basis of conventional electrochemical methods. However, the classical four electrode equipment has certain limits; such as: ionic conductivity is too big, it cannot overcome the drop of potential efficiently and it can hardly investigate the big protein [19]. The problem with the drop of potential through the surfaces was not solved until SEM was adapted to the study of charge transformation by Bard and others in the 1990s [20-24]. SEM gains an advantage over other methods in some ways. It resolves many of the difficulties associated with traditional electrochemical methods including the IR drop,

charging current and distinction between electron transfer and ion transfer etc. [25-28]. Bard *et al.* studied reverse electron transfer reaction under the ion induction through liquid/liquid interface by adapting SEM. Bard *et al.* then proved in a certain low potential range, general ET theory applicable to liquid/liquid interface, as for the higher driving force, Marcus inverted region was observed for heterogeneous ET at a modified phospholipids liquid/liquid interface [29-32]. Shao *et al.* [33] and cooperates also observed convert region behaviour at an unmodified interface. However, the flaws of SEM are that it needs to extract kinetic information from comparisons of the experimental data with an analytical approximation [34].

2. Thin-layer cyclic voltammetry (TLCV)

In 1998, Shi and Anson applied a related but less complex approach by coating a thin layer of an organic solvent on the electrode surface to examine the electron transfer process between the thin layer and the adjacent aqueous solution. This method overcomes the effect from IR drop efficiently and it is a new approach that is prompt, simple and costless. Based on the experiments, they drew some conclusions about the novel styles. Shi and Anson measured liquid/liquid interface electron rate constants that emerged from electro active substance between 1,3-diferroceny 1-2-buten-1-one (DMFc) in the organic phase and $Ru(CN)_6^{3-/4-}$ or $Mo(CN)_8^{3-/4-}$ or $Fe(CN)_6^{3-/4-}$ located in the adjacent aqueous phase. They compared the results with values that the SEM was used and found that the two pairs of data differ by less than one order of magnitude. It is possible that they used various types of organics in the solution that led to a distinct value. After that Shi and Anson discussed in detail about limit-boundary conditions in the aqueous phase and elicited upper and lower limits of concentration. In this upper and lower range, the reactions can avoid shifting the quantity through cross-phase to render the reactions reach balance [35-39]. In this way Schloz *et al.* [40] measured standard Gibbs free energy of organic anion. Shao *et al.* [41] studied ion and electron transfer through the liquid/liquid interface with a three-electrode potentiostat and results corresponded with the four–electrode potentiostat. Lu and his cooperations [42-44] using thin layer CVs (TLCV) and SEM researched in depth electron transformation behaviors through liquid/liquid interface. It proves that TLCV is practical and reliable. Above researches are all based on the single-step electron transfer oxidation.

With the development of the experiments, TLCV is used to study multi-step electron transfer. By this method, Xu *et al.* [45] and his coworkers discussed behavior of 1,3-diferrocenyl-2-buten-1-one (DFcM) with two electrochemically nonequivalent redox centers to study electron transformation reactions at liquid/liquid interface. Previously, by SEM, Bard *et al.* [46] had used glass micropipette tips to measure electron transfer at the interface between two immiscible electrolyte solutions for imaging. Similarly, by TLCV, after glassy electrodes replaced graphite electrodes, Ohsaka [47] measured kinetic parameters of multi-step redox reaction of 2,3,6,7,10,11-hexaphenyl-hexazatriphenylene (HAT). Yu *et al.* [48] studied multi-step electron transfer procedure and found out its reaction mechanism of 1,3,5-triferrocenylbenzene (TFcM). Later, Yu *et al.* [49] measured multi-step electron transfer kinetic parameters of the three –DFcM , TFcM and MFcB , comparing their properties together by using TLCV. Recently, Lu *et al.* [50] and his cooperators studied the system of two-step electron transfer of ZnTPP/ $[Fe(CN)_6]^{4-}$ by experiment and numerical simulations. The data of the experiments revealed that TLCV is better and clearer than the other traditional CVs methods. Although TLCV used in multi-step electron transfer have turned over a new leaf, nowadays, TLCV is still respected to further develop.

2.1.1. The fundamental principles

A configuration is shown schematically in Figure 1 [51]. The cells comprised of pyrolytic graphite electrode (EPG), Pt counter electrode, and reference electrode (Ag/AgCl). They are all immersed in the aqueous. The working electrode is hydrophobic EPG electrode, whose surface is polished smoothly. Drop small volumes of organic liquids on the EPG electrode surface, which spread spontaneously across their surface to produce a thin (10-100 μm) adherent layer of organic phase. The electrode is then inverted immediately and vertically immersed in the water. Thus, the ITIES is formed [52].
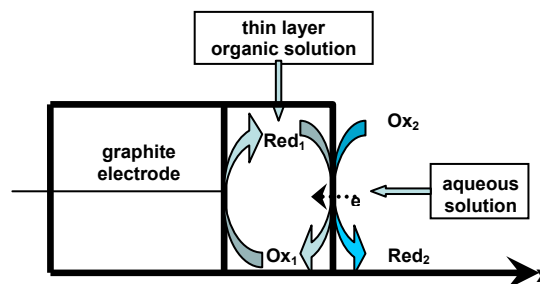

Figure 1. Schematic diagram of the electrochemical cell using thin-layer voltammetry.

Organic layer that is adhered to an electrode contains a redox-active specimen, OX_1 and aqueous phase contains a second redox-active specimen, OX_2. A bare edge-plane pyrolytic graphite (EPG) electrode, which is coated with the thin layer, is immersed in the immiscible aqueous solution contained in the oxidized form of a second redox couple, OX_2. The organic film covered on the electrode prevents the hydrophilic specimen, OX_2, in the aqueous phase from being directly reduced on the pyrolytic graphite (EPG) electrode. In other words, OX_2 in the aqueous phase cannot transfer through the liquid/liquid interface. Neither can OX_1 in the organic phase. The redox occurs between liquid/liquid phase-cross interface. The reaction equations are as follows:

$$OX_1 + e \rightarrow Red_1 \text{ (EPG)} \tag{1}$$

$$Red_1 + OX_2 \rightarrow OX_1 + Red_2 \text{ (ITIES)} \tag{2}$$
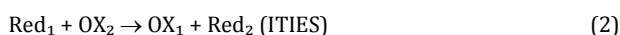
The organic layer OX_1 that can be reduced at the electrode generates the reduced form Red_1, prior to the voltammetric scan from the oxidation of Red_1 at the initial potential. Then another redox reaction can occur between Red_1 and OX_2. A feedback cycle is established in which OX_1 is regenerated in the organic phase, at the ITIES, and can diffuse back to the electrode, enhancing the current signal. The reaction is called heteropical electron reaction.

2.1.2. Rate constant

What is the relationship between electron transfer and the important parameters? Previously, Shi and Anson [53] devised the settings and did many experiments to measure current of plateaus, calculate rate constant and draw some conclusions about TLCV. Anson pointed out the cathodic plateau currents i_{obs} is composed of steady-state diffusion-limited current i_D and cross-phase reaction kinetic current i_{ET} [equation (4)] and he came up with three basic equations that hold up the thin-layer cyclic voltammetry. With the help of the formulas, we can calculate rate constant about the electron transfer reactions:

$i_D = n.F.A.C^*_{OX1}.D_{OX1}/d$ (3)

$i_{ET} = n.F.A.k_{ET}.C^*_{OX1}.C^*_{OX2}$ (4)

$$\frac{1}{i_{obs}} = \frac{1}{i_D} + \frac{1}{i_{ET}}$$ (5)

where i_D is the observed steady-state diffusion-limited current, and i_{ET} is the "kinetic current", i_{obs} is the plateau current, n is the number of electrons involved in the electrode reaction, F is Faraday's constant, and A is electrode area. C^*_{ox1}, C^*_{ox2} are the initial bulk concentration of the reactants, respectively, D_{ox1} is its diffusion coefficient, and d is the thickness of the thin layer; K_{ET} is the bimolecular rate constant for the redox reaction at the ITIES. The neutralization titration proved that between organic phase and aqueous phase are in the state of electroneutrality at steady-state current. This means there is no ion transport at the phase-cross and removed electrons at the NB/H_2O interface and the H_2O/auxiliary electrode interface have the same rate. In the state of steady-state current, the total current is controlled by the diffusion current in the NB phase. The plateau current remains essentially unchanging, so we can now measure the rate constant. The way to measure the rate constant is following:

First of all, the formulas (4) and (5) into formula (3) can get the formula (6).

$(i_{obs})^{-1} = d/(n.F.A.C^*_{OX1}.D_{OX1}) + (n.F.A.C^*_{OX1}.C^*_{OX2})^{-1}.K_{ET}^{-1}$ (6)

The diffusion coefficient, D_{OX1}, is measured by a thin layer of organic solvent that is applied to the surface of a bare electrode (often using a bare electrode covered with the nitrobenzene solution with ferrocene). Moreover, the value i_{obs} can be read from plateau current directly. The initial bulk concentration of the reactant, C^*_{OX1}, have become known. Thus, i_D can calculate easily. According to the equation (6), the plot of $(i_{obs})^{-1}$ vs $(C_{OX2})^{-1}$ should be linear, draw the point diagram then fit it to a line with a reciprocal to $(n.F.A.K_{ET}.C^*_{OX1})$ and with an interception of the line equal to $(i_D)^{-1}$. After getting the line, we can calculate $K_{et} = (n.F.A.C^*_{OX1}.k)^{-1}$ (k = slope). Experiments Testify, a plot of $(i_{obs})^{-1}$ vs $(C_{OX2})^{-1}$ can be received unless the ratio of i_{obs}/C^*_{OX2} is smaller than a certain value. The ratio for classical 10-methyl ferrocene/iron hydroxide system is around 40 μA. Different systems have unfamiliar results.

2.2. Steady-state current

At the steady-state current, the thin layer cyclic voltammetry method is mainly used to discuss important parameters. For example, rate constant, and the study of how the driving force takes effects on the electron transfer. We will elaborate on how we can gain stable current and how the driving force takes effect on the rate constant.

2.2.1. Concentration ratio

Barker and Unwin [54] simulated the thin layer cyclic voltammetry, pointing out that it is $k_r = C^*_{OX1} / C^*_{OX2}$ that cannot be neglected. If the steady-state current rises to a maximum value, it will lean on the values of K_{ET} and $k_r = C^*_{OX1} / C^*_{OX2}$. According to various kinetic reactions, we should use different k_r. Only then can we get efficient steady-state current. Comparing faster kinetics to slow kinetics, employing lower k_r may be more advantageous for the attainment of a steady-state current for the measurement of faster kinetics, because there is little kinetic barrier for ET at the ITIES and the observed current that is only limited by the diffusion rate from the specimen in the thin layer. As for moderately fast kinetics, in order to gain steady state current, the limit of k_r is significant. The valid concentration ratio is approximately $k_r \geq 20$ in the solution. Keeping the concentration of redox reactions in the H_2O/NB a certain value, and changing a variety of supporting electrolytes, Shi and Anson [55] measured the plateau current hardly changes. Keeping the concentration of supporting electrolytes constant, with the concentration of redox reactions in the water/NB ascending, their plateau currents increase slowly. Continuously, change the concentration from a larger value to a site value, their plateau currents show from a slight increase to an unchanging plateau current. Even the plateau current becomes irrelevant to the concentrations as they are high enough. The organic thin film, d, is ranged from 10 to 100 μm.

2.2.2. Limited boundary conditions

In order to attain steady-state current, thin layer method needs some limited conditions. If reliable values for i_k want to be acquired, two conditions must be met

i) The measured current, i_{obs} must be much smaller than i_D (otherwise, mass transport within the thin layer dominates the response obtained)

ii) The concentration of the reaction in the aqueous phase at the liquid-liquid interface must not be excessively decreased from its bulk of solution by the cross-phase reaction (otherwise, mass transport in the aqueous phase will affect the response obtained). It is necessary for reducing the effect of the mass transfer factor to limit the boundary conditions. A reasonable constraint to meet the first condition is $i_{obs} \leq 0.8\ i_D$. This inequality combines with equations 1-3, leading to

$(4.D_{OX1}/d.K_{ET}) \geq C^*_{OX2}$ (7)

To meet the second condition, an appropriate constraint is

$((C_{aq})_{x=0})/(C_{aq}) \geq 0.8$ (8)

where $(C_{aq})_{x=0}$ and C_{aq} are the concentration of the reactants in the aqueous phase at the liquid/liquid interface and the bulk of the aqueous phase, respectively. Finally, Anson draws a conclusion about upper and lower limits on C^*_{OX2}.

$[(4D_{OX1})/(d.K_{ET})] \geq C^*_{OX2} \geq [(8\ C^*_{OX1} . D_{OX1} . t^{1/2})/(d(\pi. D_{OX2})^{1/2}]$ [56]. (9)

All the parameters have been defined like equation 6. Experiments have verified it crucial to restrict the inequality. Only if complying with the restrictive range, we can acquire steady state currents from which reliable values of rate constant can be derived.

2.2.3. Scan speed

Barker and Unwin [57] changes scan speed again and again to measure the relationship between scan speed and kinetics by using simulation voltammeter method. He discovered, high peak current value emerges quickly and it is difficult to get steady-state current at faster scan speed. With the gradually decreasing scan speed to some certain values, the high peak current dies out and vanishes at the same time of the plateau current, finally, taking place of the peak current. Therefore decreasing the concentration of the oxidation in the aqueous phase and scan speed can improve accuracy of plateau current values and the precision of the scan plot to faster kinetics. Nevertheless, under the high concentration of the oxidation in the aqueous phase condition, the only answer has access to steady-state current in decreasing scan speed. For fast kinetics, the slow scan speed can make the current rise to a plateau value. For faster kinetics, choosing a moderate scan speed to enable a plateau current value can becomes more accessible. To

sum up, using slow scan speed is suitable for attaining steady-state current.

2.2.4. Thickness

Barker and Unwin points out the thinner the thin layer is, the higher the platform is in the experiment of simulated thin layer cyclic voltammeter [58]. This conclusion is similar with the results of other methods. In the course of experiment, we found, thickness makes much more difference to measure electron transfer and have complicated impact on it. It is apparent that the thickness is associated with the accuracy of rate constant.

We can calculate thickness just before plateaus current emerges by choosing such a fast scan speed that the thickness of the diffusion layer is quite smaller than the thickness of thin layer. The peak current is controlled by diffusion and now the current is independent of its thickness. The values of the current can be calculated using different peak current ratios with such scan speeds [59]. The thickness is computable as following:

$$D = 0.286.D_{0X}^{1/2}.R_i.\upsilon_t^{-1}.\upsilon_d^{1/2} \text{ [60]}. \tag{10}$$

where R_i is the ratio of the peak currents. υ_t and υ_d are respectively diffusion-limited responses of scan speed. Others are the same above. The process of electron transfer through liquid/liquid interface is a rapid reaction, which is subjected to controlling from the diffusion speed in the organic phase while it lies in stable plateaus current. On one hand, the thinner the layer is, the higher the concentration gradient between EPG electrode and ITIES is, thereby, having faster ion transfer rate we can obtain more currents. On the other hand, thickness of the thin layer does not affect observation under the unsteady-state. As is evident, the procedure of the electron transfer is mainly controlled by the rate of electron transfer of interface NB/H_2O. This research is also helpful to overwhelmingly understand the "Marcus inverted region theory".

2.3. Mainly factors that effect rate constants

The rate constant for the electron transfer reaction at the ITIES is mainly determined by the three parameters, namely, reorganization of energy (λ), difference between the formal potentials of the two redox couples in their respective phases (ΔE) and the Galvani potential difference ($\Delta_w^o\Phi$).

2.3.1. Driving forces

The overall driving force for the reaction through the liquid/liquid interface which is composed of the difference, ΔE, between the formal potentials of the two redox couples in their respective phases and $\Delta_w^o\Phi$, which is the Galvani potential difference at the liquid/liquid interface [61]. The value of $\Delta_w^o\Phi$ can be easily changed by adjusting the concentration of the potential-determining ion (e.g., ClO_4^-, an ion that moves across the liquid/liquid interface). An alternative approach to change the overall driving force is the use of different redox couples either in the aqueous phase, or in the organic phase. Anson adds driving force step by step by changing electro active reactant in the organic phase or by changing pH of the aqueous phase to measure the change of ket in organic phase using thin layer method. Therefore, that the study of the driving force depends on electron transfer kinetics through the ITIES has been largely focused on the modulation of $\Delta_w^o\Phi$ at the interface. The results show that it is essentially insensitive for rate constants of ET at ITIES to depend on the potential applied across the interface. However, improving driving force further, liquid/liquid interface may be entered into the inverted region

of Marcus theory [62], which is also observed by Bard and others. Results indicate the values of k_{et} decrease with the values of $\Delta_w^o\Phi$ increasing high enough, which is not in agreement with previous conventional Bulter-Volmer treatment. When the concentrate in the organic remain constant and the concentrate in the aqueous changes, the experiment results show that if the ratio $k_r = C^*_{0X1}/C^*_{0X2}$ increase per decade, the potential will be in the range of 30-34 mV [63]. Yu *et al.* [64] observed the direct correlation between driving force and liquid/liquid interface electron transfer rates. Shi and Anson measured rate constant by using multiply charged anions in the aqueous phase and just only using decamethy ferrocene in the organic phase. Results show k_{et} change with different charged anions in the very dilute supporting electrolytes but it becomes less dependent on changing $\Delta_w^o\Phi$ as each supporting electrolyte concentrate increases [65]. Mirkin studied electron transfer by SEM, and found the ET rate is essentially independent of the potential drop across the interfacial boundary [66]. By using SEM, Mirkin and Murray measured the fast electron transfer dynamics at a liquid/liquid interface and found that the dependences of the effective heterogeneous rate constant on the concentration of the aqueous redox mediator and reaction driving force were found to be in agreement with theoretical expectations [67].

2.3.2. Reorganization energy

λ is the reorganization energy, which is defined as the reversible work necessary to change the solvent polarization from the one corresponding to the solvent equilibrated to the reactants to that when the solvent is at equilibrium with the products. The reorganization energy may be contributing to more effect on ket than driving force. Liu *et al.* [68] substitutes Fe^{3+} with $Fe(CN)_6^{3-}$ in the aqueous phase and proves the results that the driving force increases, the rate constant has a little decrease. Thus shows the ket may be much more sensitive in reorganization energy than driving force. Reorganization energy may have major effect on ET. It can increase activation of energy.

3. Summary and future outlook

It is very important to study liquid/liquid interface for ET. ET is closely connected with biomembrane of life science. Using TLCV method can efficiently measure ET across liquid/liquid interface. By trial and error, researchers have further developed TLCV method. Of course, the disadvantage of theories hinders the development of the method .The effects of driver force on thin layer need a set of better theory. However, this simple and efficient method is worthing widely using in our experiments. Recently, the thin layer method has largely drawn people's eyes to measure multi-step ET. The experiments and theories have being widened not only in one single-step ET but in multi-step ET as well. We expect to perfect the simulation between driving force and k_{et} in multi-step ET. Prompting the thin layer method could better serve the world of life science.

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