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Determination of Diffusion Coefficient and Number of Electrons Transferred Through Ultramicro Platinum Electrode

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This study aims to introduce the cyclic voltammetry (CV) with ultramicro platinum electrode technique, enable their comprehension through starting from the known conventional CV method and determine the differences between the conventional CV and the cyclic voltametry with ultramicro platinum electrode. The CV obtained through the usage of micro electrode and the voltammograms obtained through the cyclic voltametry with ultramicro platinum electrode were compared and contrasted. The diffusion coefficient (D) and the number of electrons transferred (n) were calculated with the help of the CV results obtained through the utilization of chronoamperometer and ultramicro platinum electrode. In this study, using the ultramicro platinum electrode, the diffusion coefficient of the azobenzene was calculated as $9.89 \times 10^{-6a} \pm 8.17 \times 10^{-7}$ and that of ferrocene was calculated as $1.12 \times 10^{-5} \pm 4.69 \times 10^{-7}$. The number of electrons transferred for both substances was found to be 1.

Key Words: Ultramicro platinum electrode, Diffussion coefficient, Cyclic voltammetry.

INTRODUCTION

Today, there are many theoretical and practical studies in the field of electro chemistry, which have many essential academic contributions. The main discussion topics are how much the taught knowledge at laboratories or classrooms at graduate or postgraduate level are learnt by the students; whether their importance is well-comprehended and to what extent the developments could be revealed. It is very important for the students to be aware of the scientific developments as teachers follow them and share with their students. In order to address these problems a study called Australian Physical Chemistry Enhanced Laboratory Learning (APCELL)[1] was started in Australia in 2000. One of the primary objectives of the APCELL project is to disseminate widely the results, outcomes and practical developments in physical chemistry laboratory exercises that are based upon student-focused pedagogical tenets. The APCELL project has focused upon addressing one important aspect in improving student motivation and learning in physical chemistry-the student laboratory experience. Laboratory work is considered to be of great importance in the chemistry curriculum, yet research suggests that it may not achieve the desired learning objectives[2,3]. Students can often see the laboratory exercise as simply a task to be completed as quickly as possible, with the minimum possible effort[4] and this attitude can defeat any attempts to use the experience as a teaching and learning tool.

In this study, this reality was taken as basis and ultramicro platinum electrode was chosen as the topic, since it allows the utilization of laboratory environments as teaching and learning tools.

This study is not an APCELL project study; however, it is designed by taking into consideration the issues indicated by the APCELL project. The essence of the study comes from its contributions to the comprehension of the importance of the data collected at laboratories as well as the reflection of microscopic events that occur during the acquisition of these data on the students and its emphasis on the importance of how these data could be used in other fields with various aims. This study aims to introduce the students the cyclic voltametry with ultramicro platinum electrode technique, enable their comprehension through starting from the known conventional CV method and determine the differences between the conventional CV and the cyclic voltametry with ultramicro platinum electrode. The CV obtained through the usage of micro electrode and the voltammograms obtained through the cyclic voltametry with ultramicro platinum electrode were compared and contrasted. The diffusion coefficient (D) and the number of electrons transferred (n) were calculated with the help of the CV results obtained through the utilization of chronoamperometer and ultramicro platinum electrode. Although numerous undergraduate-level experiments are available for cyclic voltametry[5-15] none have addressed the topic of ultramicro electrode techniques[16]. The utilization of ultramicro platinum electrode in electro chemistry has a history of 25 to 30 years and has much superiority in terms of its utilization characteristics. Some of these could be listed as follows: Ultramicro electrodes are much less susceptible to the severe distortion caused by uncompensated resistance or ohmic drop. This has opened new opportunities for cyclic voltammetric studies in poorly conductive media, such as nonpolar solvents, polymers and other rigid matrices. The effects of high solution resistance can be observed by limiting the supporting electrolyte concentration in an electrochemical cell. Because the supporting electrolyte is crucial for increasing the ionic conduction in solution (and repressing the migration of electro active species), it is typically used in large excess relative to the substance being studied. In a strict sense, cyclic voltametry is impossible in the complete absence of supporting electrolyte[16]. Ultramicro electrodes are much less sensitive to large solution resistance because the value of iRu is relatively insignificant given the extremely small currents that are generated. Thus, even at very low electrolyte concentrations there is still sufficient ionic conduction for a successful experiment[16].

The CV study by Stanton *et. al.*[16], where the ultramicro electrode was used, created an important perspective upon the topic. The study involved important theoretical knowledge related to the topic[16]. This study was designed by taking into consideration some principles of the Research-led teaching (RLT) technique, which is mentioned in the APCELL project. Therefore, "the use of disciplinary research in teaching" and "teaching and curriculum that uses evidence derived from research and inquiry" as main aspects of the technique formed the directing dimensions of the study, as they also were in the study by Stanton[16] in terms of laboratory experiment suggestion. Additionally, students would be benefiting from a scientific study while a laboratory study is being processed.

EXPERIMENTAL

The molecular structure of the investigated compound is given as below (Fig. 1).

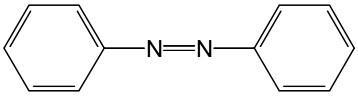

Fig 1. Structure of azobenzene

The substance could easily be obtained commercially.

Dimethylsulfoxide (DMSO) used was an absolute dry (water ≤ 0.01 %) batch of Fluka (41648) kept on beads of a molecular sieve (4 Å). Ferrocene-ferrocenium redox couple was used as a reference matter in non-aqueous media.

The supporting electrolyte, tetrabutylammonium tetrafluoraborate (TBATFB) was purchased from Fluka (21,796-4) and was used without purification. All of the other chemicals were of reagent grade and used without further purification. 1.0×10^{-3} M solution for the voltammetric studies were prepared dissolution of an appropriate amount of solid azobenzene in dimethylsulfoxide containing 0.1 M TBATFB.

The voltammetric experiments were carried out using a computer controlled electroanalysis system which is BAS 100B Electrochemical

Analyzer. Platinum electrode (BAS MF-2013) and 100 μm-ultramicro platinum electrodes (BAS MF-2150) were used as a working electrode. A platinum wire (BAS MW-1034) was used as the auxiliary electrode. The reference electrode was a silver wire in contact with 0.1 M $AgNO_3$ in dimethyl sulfoxide. All solutions were deaerated for 10 min with pure argon. All the measurements were taken at room temperature, 20 ± 1 °C.

The number of electrons transferred and diffusion coefficients were determined by the conventional CV and ultramicro platinum electrode CV technique of Baranski[17].

RESULTS AND DISCUSSION

At the first stage of the study, the cyclic voltammograms obtained through the utilization of micro (conventional) and ultramicro platinum electrode were compared and contrasted. In experiments with normal time scales, cyclic voltammograms obtained with ultramicro electrodes differ significantly from those obtained using electrodes of conventional size. This is due to the differences in mass transport within the diffusion layer, the region adjacent to the electrode in which electrolysis takes place. At large electrodes, mass transport occurs mostly perpendicular to the surface (planar diffusion). The result is a typical peak-shaped voltammogram[18,19].

Cylic voltammogram of the solution containing 1×10^{-3} M of azobenzene at a scan rate of 0.1 Vs^{-1} are shown in Fig. 2. The reduction of compound in DMSO containing 0.1 M TBATFB proceeds in one step. The only one cathodic peak (Ic) present at -1770 mV.

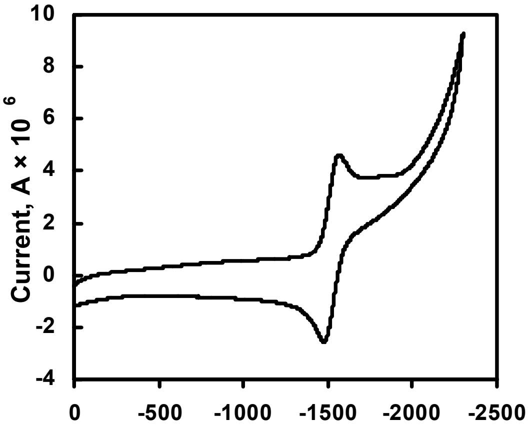

Fig. 2. Cyclic voltammogram of 1×10^{-3} M azobenzene in dimethylsulfoxide containing 0.1 M tetrabutylammonium tetrafluoroborate at a scan rate of 0.1 V/s

By contrast, mass transport at ultramicro electrodes takes on a hemispherical profile (radial diffusion). This produces a sigmoidal, steady-state voltammogram[19-22]. Unlike the situation for a Standard size electrode, currents generated at ultramicro electrodes are dependent on their geometry. For a disk-shaped electrode, the limiting plateau current from CV is given by eqn. 1, in which i_{lim} is limiting current (A), F is Faraday's constant and r is electrode radius (cm)[20]. For a conventionally-sized electrode, the current is proportional to electrode area, but is not geometry dependent.

$$i_{lim} = 4nFrDC^{o} \tag{1}$$

Fig. 3 displays the cyclic voltammograms of the 1×10^{-3} M azobenzene and ferrocene at ultramicro platinum electrode.

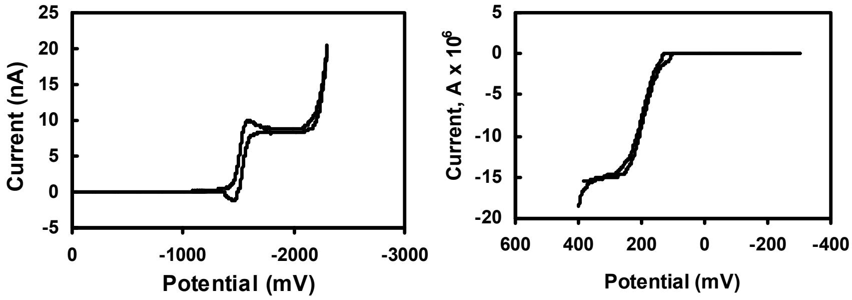

Fig. 3. Cyclic voltammogram of 1×10^{-3} azobenzene and ferrocene in dimethysulfoxide containing 0.1 M tetrabutylammonium tetrafluoroborate at ultramicro platinum electrode at 10 mV s^{-1} scan rate

The obtaining of voltammograms and their discussion with students are important since they allow the observation of the differences between the CVs obtained through micro and ultramicro platinum electrodes. In this way, the concepts become more meaningful.

Calculation of n and D values: The number of electrons transferred at the heterogeneous reactions at electrode level for azobenzene was calculated according to the technique used by Baranski and his colleagues[17]. In this technique the number of electrons transferred and the diffusion coefficient could be calculated through the utilization of micro electrode and the ultramicro electrode. Baranski *et al.*[17] reorganized the Cottrell equation and the equation that explains the border flow for the ultramicro electrodes for a substance, the number of analyte and electrons transferred of which are known. They produced the following equations (eqn. 2 and 3).

$$n = \frac{n_s S^2 i_s C_s}{S_s^2 i C} \tag{2}$$

$$D = \frac{D_s S_s i^2}{S^2 i_s^2} \quad (3)$$

here, i is the steady-state current, C is the concentration; S is the slope of the Cottrell plot for azobenzene. On the other hand is, C_s and S_s are the same terms but for ferrocene which was selected as a standard system.

This technique has the superiority that it does not require the calculation of the active surface area of the micro electrode and it reaches to accurate conclusions. The reason why ferrocene is used as the standard substance is because this component provides a clear reduction of 1 electrode and its resolution is high. The chronoamperometer (CA) experiments were done in order to calculate the Cottrell slopes of the azobenzene and standard ferrocene component and the peak potentials determined at CV experiments were taken as basis. The slopes of the i-$t^{½}$ graphs obtained as a result of these experiments and their correlation coefficients were recorded. The results are displayed in Table-1.

TABLE-1
CHRONOAMPEROMETER RESULTS OF AZOBENZENE AND FERROCENE AT ULTRAMICRO PLATINUM ELECTRODE IN DMSO ENVIRONMENT

Azobenzene		Ferrocene	
$S_{cotrell}$	R	$S_{cotrell}$	R
8.784×10^{-5}	0.97	1.17×10^{-4}	0.99
8.793×10^{-5}	0.98	1.14×10^{-4}	0.99
8.560×10^{-5}	0.97	1.15×10^{-4}	0.99

Using the data in Table-1, the D and n values for azobenzene and ferrocene-ferrocenium were calculated. As shown in the Table-2, the number of electrons transferred related to reduction peak for azobenzene and ferrocene-ferrocenium couple were found to be 1.

TABLE-2
DIFFUSION COEFFICIENT, THE NUMBER OF ELECTRONS TRANSFERRED CALCULATED FOR AZOBENZENE AND FERROCENE

Compounds	D ($cm^2 s^{-1}$)	Number of electrons transferred for azobenzene (n)
Azobenzene	$9.89 \times 10^{-6a} \pm 8.17 \times 10^{-7a}$	0.81 ± 0.03
Ferrocene	$1.12 \times 10^{-5} \pm 4.69 \times 10^{-7a}$	1.00

[a] Standard deviation for three results.

From the perspective of the graduate level, the most charming aspect of the ultramicro platinum electrodes is their quite small sizes. Even spending some time for the visual observation of the electrodes is essential. Although the 50 and 25 μm discs could be seen with naked eye, a microscope or a magnifying glass is required to see a disc with 10 μm diameter. As an advantage of this small size, the ultramicro electrodes could be utilized in experiments that require electro chemistry in small or microscopic environments. For example, especially in medicine, they were used for the observation of dopamine dynamics, which are electroactive neurotransformators in or around the brain tissue[21]. In this study, using the ultramicro platinum electrode, the diffusion coefficient of the azobenzene was calculated as $9.89 \times 10^{-6a} \pm 8.17 \times 10^{-7}$ and that of ferrocene was calculated as $1.12 \times 10^{-5} \pm 4.69 \times 10^{-7}$. The number of electrons transferred for both substances was found to be 1. Laviron and Mugnier[22] studied the electrochemical reduction of *cis*-azobenzene at dimethylformamide with polarographic, controlled potential coulometry and cyclic voltametry and they concluded that the *cis*-azobenzene radical anion obtained in the first 1e stage isomerizes rapidly to the *trans* anion. The results of the above-mentioned study are in line with the conclusions come in this study.

In the study, the cyclic voltammograms of azobenzene obtained through the cyclic voltametry with the utilization of microelectrodes and ultramicro platinum electrodes were compared and contrasted. With the help of the data acquired from the CV studies with the utilization of ultramicro platinum electrodes and chronoamperometer, the diffusion coefficient and the number of electrons transferred were calculated. This study is important since it indicates that the diffusion coefficient could be calculated through the utilization of ultramicro platinum electrode. By performing such a study in the laboratory environment and creating a working environment in line with RTL enabled students to explore new things in the light of the scientific data. This indicates the importance and permanence of the study. This is a student-centered study and its findings are original. Students could feel themselves as scientists and see their work as a contribution to science. Therefore, they would stop seeing labs as places where things that should be completed as quickly as possible are done. It is clear that in an environment where students with such attitudes are present, it is not possible to utilize laboratory experiments as teaching and learning tools.

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