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Determination of the Standard Heterogeneous Rate Constant Through Scientific Research in Teaching

NILGÜN SEÇKEN
Department of Chemistry Education, Faculty of Education
Hacettepe University, 06800 Beytepe, Ankara, Turkey
E-mail: nsecken@gmail.com

In this study, the cyclic voltammetry data obtained in laboratory environment through the determination of standard rate constant (k_s) of the electron transfer with the help of cyclic voltammetry. At graduate level, when it comes to rate and rate constant, students mainly think of chemical reaction rates. However, emphasizing that there are rates that belong to the electron transfer at electrochemical reactions would enable students to look at electrochemical events through a different perspective. The importance of this study stems from its effect on students' comprehension that in electrochemical events, electrons have certain rates. The present study concerns with the determination of standard rate constant k_s in an ethanol-water (1:5 v/v) mixture. In the light of the information attained from the literature, the k_s calculation was done and the rate constant of the electron transfer was calculated together with the students.

Key Words: Rate constant, Cyclic voltammetry, Nicholson, Laboratory instruction, Electroanalytical techniques.

INTRODUCTION

Nowadays, there are many theoretical and practical studies on electrochemistry, which have important academic contributions to the field. However, how much of the knowledge taught at classrooms and laboratory environments are learnt by the students, whether its importance is well-understood and to what extent the developments are reflected are still matters of discussion. A project study called Australian Physical Chemistry Enhanced Laboratory Learning (APCELL) was started in Australia in 2000 in order to solve the problems related to these issues[1]. The aim of this project could generally be summarized as follows:

The APCELL project was established to use the context of laboratory learning to address the problem of low intake and poor retention of students in Australian physical chemistry courses. 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 project's genesis, however, can be traced back several years earlier to discussions between academicians attending research conferences around Australia, concerning anecdotal evidence that an increasing number of students were finding their physical chemistry laboratory courses to be boring and discouraging. These informal discussions highlighted a widespread recognition amongst academics that students studying physical chemistry were not learning in the laboratory as well as they should, or could. 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.

This study is not an APCELL project study; however, the points indicated by the APCELL project were taken into consideration. This is in essential study since it enables the comprehension of data collected at laboratories, promotes the recognition of the microscopic events at reactions that occur during data acquisition, emphasizes the importance of the utilization of these data in other field with various aims and provides the active parti-*cipation of all students at the process and evaluation stages.

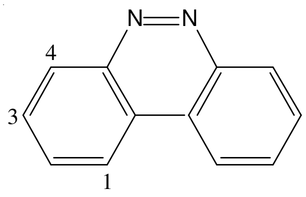
In the study the cyclic voltammetry (CV) data obtained in laboratory environment through the determination of standard rate constant (k_s) of the electron transfer with the help of CV. This is an important issue because; at graduate level, when it comes to rate and rate constant, students mainly think of chemical reaction rates. However, emphasizing that there are rates that belong to the electron transfer at electrochemical reactions would enable students to look at electrochemical events through a different perspective. The importance of this study stems from its effect on students' comprehension that in electrochemical events, electrons have certain rates. When performing CV studies in laboratory environments, the primary action is usually to do the reversibility tests for the reaction. The cyclic voltammograms are examined and reversibility tests are done as Bard[5] indicated in order to determine if the reaction is reversible, irreversible or quasi-reversible. Following the determination of the possible chemical reactions that may court electrochemical reaction, their mechanisms and surface reactions are tried to be explained. Nevertheless, there are not many educational studies on kinetics, since they are secondary duties. Here, a question arises: Is the recognition and comprehension of kinetics knowledge are important in chemical education? This is very important aspect, because, electrochemical events are not simple reduction-oxidation events. When a reduction-oxidation event occurs, this involves many microscopic events as well as data/information to be used in their explanations. It is essential for the students to comprehend the importance of these microscopic events and be acknowledged about the developments in order them to feel themselves involved with science. Because if a student is treated as an individual working like a scientist, then not only his/her motivation would increase but also his/her perspective would change. As well, in APCELL project, there is an emphasis on the Research-Led Teaching (RLT). The term RLT has various meanings in different contexts[6]. Amongst other things RTL can refer to: (a) the use of disciplinary research in teaching-for example, the use by a teacher of one of their current journal publications reporting a key piece of cutting edge research; (b) teaching and curriculum that uses evidence derived from research and inquiry-for example, designing a learning task on the basis of published education research or one's own inquiries into how students approach particular assessment tasks; (c) research into teaching and learning for example, a research investigation into how students approach different learning tasks.

Taking these criteria into consideration, in this study the standard rate constant (k_s) calculation was done for the first reduction peaks of the 1-bromobenzo[c]cinnoline, 3- bromobenzo[c]cinnoline and 4-bromobenzo[c]-cinnoline, which are obtained using the CV technique. CV is a versatile electrochemical technique, its principles and theories have been discussed by Kissinger and Heineman[7]. Despite the advantages of the technique and its widespread use, there is a lack of CV experiments in the literature for the students.

This study was designed by considering some principles of the Research-Led Teaching as indicated in the APCELL project.

EXPERIMENTAL

1-Bromobenzo[c]cinnoline, 3-bromobenzo[c]cinnoline and 4-bromobenzo[c]cinnoline were prepared as described by Kiliç[8] in the literature. The molecular formula of the benzo[c]cinnoline, which is the main substance of the study, is as follows:

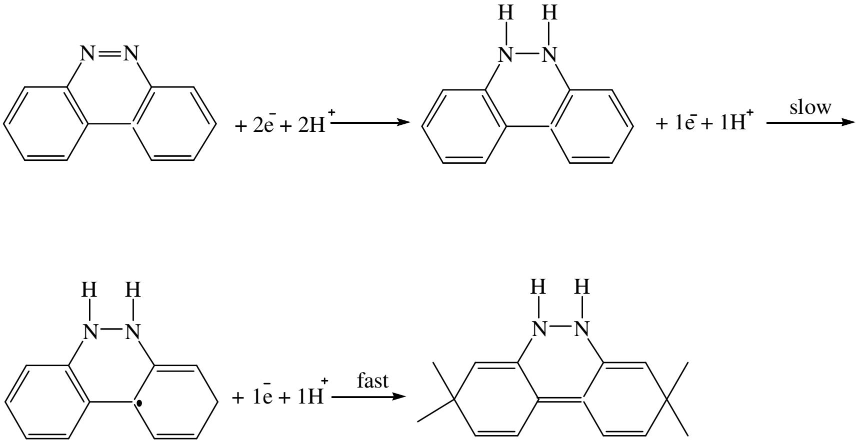


1: 1-bromobenzo[c]cinnoline
3: 3-bromobenzo[c]cinnoline
4: 4-bromobenzo[c]cinnoline

The Britton-Robinson (BR) buffer solution was used in the study[9]. While getting cyclic voltammograms, three electrode combination system was used. This consisted of a Multi Mode Electrode (Dropping Mercury Electrode, DME, Static Mercury Electrode, SME and Hanging Mercury Drop Electrode, HMDE), Ag/AgCl reference electrode and a Pt wire auxiliary electrode. Cyclic voltammogram is registered in the -200 to - 450 V range.

RESULTS AND DISCUSSION

The use of disciplinary research in teaching: Prior to the study, Chemistry Laboratory Anxiety Instrument was administered to the students. The Instrument that consisted 20 items was developed by Bowen[10] and adapted to Turkish and calculated Turkish Version's reliability by Azizoglu[11]. The Instrument was consisted of four dimensions. The reliability coefficients of the dimension were between 0.86 and 0.88. We used in our study working with other students dimension which consisted of 4 items and obtaining data dimension which consisted of 6 items through our goals. Students answered 10 items totally. The instrument was administered as post test following to the study to determine the effect of the process on students' laboratory anxiety. Later, students did a literature research on the mentions substances in the study. This process was in line with the 'utilization of scientific research in teaching' stage of the Research-Led Teaching. After the examination of the data, this basic information regarding the main substance of the study, benzo[c]cinnoline, was attained. It is known that benzo[c]cinnoline has mutagenic activity[12] and some of its derivatives have antirheumatic[13] and herbicidal activity[14]. The electrochemical behaviour of 1-bromobenzo[c]cinnoline, 3-bromobenzo[c]cinnoline and 4-bromobenzo[c]cinnoline has not been reported so far. The polarographic behaviour of benzo[c]cinnoline in acetonitrile in the presence of various proton donors such as water, phenol, benzoic acid and perchloric acid was reported. On the other hand the reduction of benzo[c]cinnoline in DMF with 0.1 M $[(CH_3)_4N]ClO_4$ as a supporting electrolyte was used to produce radicals that were detected by ESR[15]. Cyclic voltammetric behaviour of benzo[c]cinnoline on smooth platinum was studied in liquid ammonia and two reversible reduction peaks were reported[16]. The polarographic reduction of benzo[c]cinnoline on a mercury electrode was reported to be irreversible with a single two-electron transfer in 80 % aqueous alcohol[17]. The electrochemical reduction of benzo[c]cinnoline in the presence of non-reductible electrophiles in DMF, at a mercury pool cathode, was studied to synthesize various cyclic compounds[18]. In another report benzo[c]cinnolines were used as model molecules in a study to find on the general expression for the kinetics of surface electrochemical reaction, by using linear potential sweep voltammetry[19]. Benzo[c]cinnoline was reduced in Stafford buffer and showed two discrete two-electron diffusion controlled waves on a mercury electrode[20]. The expected behavioural change in students was the comprehension of the knowledge that the starting substance benzo[c]cinnoline has two reduction waves each with two electrons at the acidic environment (1:5, EtOH: BR environment) and the first reduction wave displayed quasi-reversible characteristics[20-24]. At the end of the literature studies, students learnt this information as well as the information regarding the reversibility studies of the first reduction of the substances. Additionally, the reaction mechanism given below, which was indicated in the literature studied by students, was discussed. Necessary explanations were made on some topics and concepts, which were determined to be unknown by the students (such as supporting electrolyte, scan rate, reversibility, quasi-reversible). The electrode reaction at the water environment occurs *via* the mechanism explained below:



That is how the reversibility studies and mechanism analysis as the primary duty of the cyclic voltammetry was actualized with the help of the literature. This study involves the k_s values and their calculation as the secondary duties of cyclic voltammetry.

Teaching and curriculum that uses evidence derived from research and enquiry: The present study concerns with the determination of standard rate constant k_s in an ethanol-water mixture. In the light of the information attained from the literature, the k_s calculation was done and the rate constant of the electron transfer was calculated together with the students. When studying the k_s, two literatures were especially served as guiding lecture notes for students and researchers[25,26]. Discussing these studies, doing a laboratory practice depending on these studies and planning student works in the light of a scientifically proven study had a quite positive impact on students' perspectives. That is because the data to be obtained at the end of the study would be found by them first and would contribute to science, similar to the studies in literature. Having such an experience enabled students to feel like scientist in classrooms and increased their motivation. Firstly, the cyclic voltammograms of 1-bromobenzo[c]cinnoline, 3-bromobenzo[c]-cinnoline and 4-bromobenzo[c]cinnoline taken at acidic environment were examined. The cyclic voltammograms of the substances were taken at 1:5 EtOH/BR environments in acidic pH values at 0-1 V intervals. This study displayed that there are two cathodic peaks and there is one anodic peak belonging to the substances. The 0-1 V interval was narrowed down in order to display to which cathodic reduction the anodic peak belonged. Firstly the 0-0.5 and then the 0.5-1 V intervals were examined separately. Students observed that the anodic peak belong to the first reduction. Therefore, they attained the basic knowledge related to the peak that belong to the first reduction they would study.

Fig. 1 show some typically reversible cyclic voltammograms obtained for the 1-bromobenzo[c]cinnoline, 3-bromobenzo[c]cinnoline and 4-bromobenzo[c]cinnoline in acidic environment.

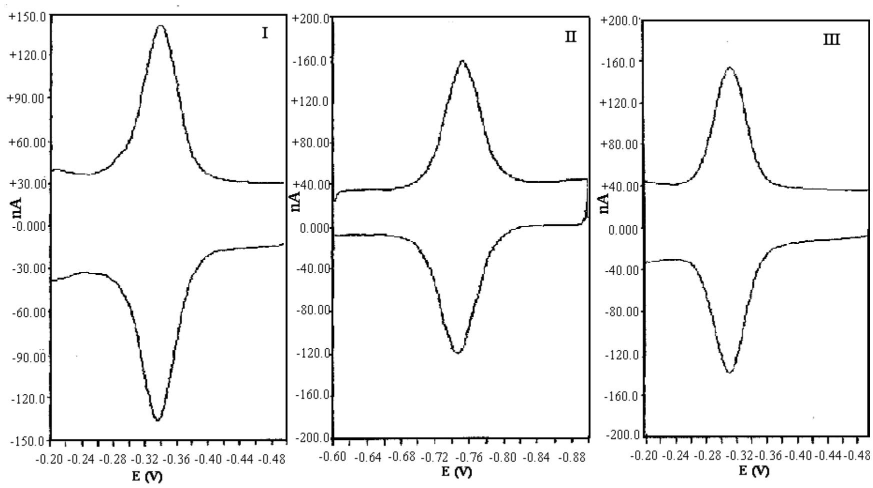


Fig. 1. Cyclic voltammograms of 1-bromobenzo[c]cinnoline, 3-bromobenzo[c]cinnoline and 4-bromobenzo[c]cinnoline at slow scan rates. Scan rate= 100 mV/s, c= 1.67 × 10^{-7} M, 1:5 ethanol + BR buffer. 1-bromobenzo[c]cinnoline (I), 3-bromobenzo-[c]cinnoline (II), 4-bromobenzo[c]cinnoline (III)

As seen on cyclic voltammograms at the acidic environment 1-bromobenzo[c]cinnoline, 3-bromobenzo[c]cinnoline and 4-bromobenzo[c]-cinnoline, within -200 and -450 mV interval, there are cathodic and anodic (first reduction) peaks. Using the changing of the potential difference between the anodic and cathodic peak potentials of the first peak with the scan rate, the standard rate constant of the electron transfer could be calculated with CV[26]. On order to calculate k_s according to the Nicholson method, there is the need for anodic peak, too. Therefore, in this study, only the data of the first peak were taken into consideration. In the light of the theoretical knowledge indicated in studies by Scmitz and van der Linde[25], which were also explained by Nicholson[26], the equalities to be used in calculation, the concepts related to these equalities and explanations related to these concepts were declared. The ψ value in equality 1 was obtained by the students with the help of the graphs suggested by Nicholson[26]. In order this graph to be utilized, the ΔE_p values at different scan rates were calculated with the help of the cyclic voltammograms. The transferred electron number was taken as 2 as the literature indicates.

Nicholson method: The k_s value of the electron transfer reaction was also determined by the use of the technique developed by Nicholson[26], using:

$$\psi = \frac{k_s}{\sqrt{\pi \alpha D_o}} \tag{1}$$

$$\alpha = \frac{nF\nu}{RT} \tag{2}$$

here, D_o is diffusion coefficient of the depolarizer, ν is the scan rate and the other symbols have their usual meaning is obtained from a ΔE_p-ψ working curve in which ΔE_p is the anodic cathodic peak potential difference, an easily measured parameter.

The standard rate constants determined by the use of these methods were found to be in good accordance with each other in certain ranges of the scan rate (Table-1).

In the literature, the studied substances were explained to be quasi-reversible. In quasi-reversible reactions, i_p increases with $\nu^{1/2}$, but this is not linear. $i_p^a/i_p^c = 1$; $\Delta E_p > 59/n$ mV; ΔE_p increases with ν and E_p^c moves to the negative value as the ν increases. Students found the chance to observe all these characteristics while they were calculating the k_s value. Additionally, the obtained k_s values are within the k_s limits indicated for quasi-reversible reactions in the literature. If the system is quasi-reversible[5], then $0.3\nu^{1/2} \geq k_s \geq 2 \times 10^{-5}$. The obtained values are within this interval and these results contributed to students' understanding the importance of their work. Therefore; a scientific study, which takes the student into the center, was completed. After determining k_s values by this way with the students, Chemistry Laboratory Anxiety Instrument was administered once more to the students as post test. The Chemistry Laboratory Anxiety Instrument is consisted of 4 dimensions, but in this study only two of them were used. The pre and post test datas were compared by paired samples t-test and the results were discussed (Table-2).

TABLE-1
k_s VALUES OF 1-BROMOBENZO[C]CINNOLINE, 3-BROMOBENZO[C]CINNOLINE AND 4-BROMOBENZO[C]CINNOLINE, WHICH ARE CALCULATED WITH THE NICHOLSON METHOD

Compound	pH	ν (V/s)	ψ	k_s (cm/s)	$X_{mean}(k_s)$ (cm/s)
1-Bromobenzo[c]cinnoline	3.36	0.7	1.02	0.047	0.0375 ± 0.0059
		0.8	0.84	0.042	
		0.9	0.59	0.031	
		1.0	0.54	0.030	
3-Bromobenzo[c]cinnoline	3.01	0.7	0.59	0.038	0.0295 ± 0.0098
		0.8	0.55	0.038	
		0.9	0.31	0.023	
		1.0	0.23	0.019	
4-Bromobenzo[c]cinnoline	3.78	0.7	0.44	0.031	0.0240 ± 0.0050
		0.8	0.32	0.024	
		0.9	0.29	0.023	
		1.0	0.22	0.018	

TABLE-2
DESCRIPTIVE STATISTICS AND PAIRED SAMPLES t-TEST RESULTS OF CHEMISTRY LABORATORY ANXIETY INSTRUMENT (n = 24)

	Mean	N	SD	SE Mean	t	df	Sig. (2-tailed)
Pre-test	35.63	24	7.90	1.61	6.75	23	0.00
Post-test	26.92	24	8.02	1.64			

It is seen that while pre-test mean is 35.63, post-test mean is 26.92. These results display that the applications which are student-centered decrease students' anxieties towards laboratory. Also difference between these findings is statically significant (p = 0.000).

Since chemistry is a domain based on experiment, laboratory is an important part of chemistry learning. Hofstein and Lunetta[27] list main aims of laboratory education like that: (1) developing interest, curiosity and positive attitude towards science, (2) obtaining creative thinking and problem solving skill, (3) developing scientific thinking, (4) increasing conceptual understanding, (5) developing application skills such as data collection, observation, interpretation of the results. There are various factors that effect attaining these aims, *e.g.*, students' attitudes towards laboratory, their anxieties, number of student, behaviour of teacher, laboratory handbook, laboratory setting. Also students feel anxious about usage of chemicals, data collection and usage of laboratory time. These anxieties towards chemistry laboratory effect students' performance[28,29]. When laboratory in science is considered as an integrant element of teaching, determination of anxiety towards science and chemistry will not enough. Generally researches about this topic have focused on science and chemistry anxiety[28,30-34]. Anxiety towards laboratory has been examined in few researches[10,28,29]. When one student who has no anxiety towards science lessons participates in laboratory, he/she develops anxiety by influence of various stimulants. Knowing of the anxiety dimension and its' source will effect on the determination of removing ways of anxiety and orientation of students to laboratory again. So the determination of students' anxieties towards laboratory is important. In the conducted study, scientific researches have been used considering these and students have conducted their studies. As a result of these, a decrease in students' anxieties towards this type of difficult laboratories has been provided.

Furthermore, the students can now think broader or they can think about microscobic level events when we talk about speed. They do not only define ‘speed’ as a distance covered by an object, but they can also think about the electron transfers in electrochemical events are occured in a definite speed.

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