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Determination of Standard Rate Constant of Azobenzene in Non-Aquaous Media

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This study suggests an experiment where the standard heterogeneous rate constant k_s can be calculated with the help of cyclic voltammetry data obtained through the cyclic voltammeter technique in the laboratory environment. Suggested experiment was consisted of 4 steps. In the first step electrode reaction was defined by using cyclic voltammetry technique. In the second step of the experiment, adsorption of azobenzene to electrode surface was searched. In the third step, necessary quantitative sizes were calculated to determine the standard rate constant. In the last step, standard rate constant was calculated by using obtained data in the previous steps. This heterogenenous standard rate constant for the reduction was calculated by Klingler Kochi technique. In this study, using the micro platinum electrode, the standard rate constant of the azobenzene was calculated as 0.0309 ± 0.002142.

Key Words: Standard rate constant, Cyclic voltammetry, Azobenzene, Rate constant.

INTRODUCTION

This study suggests an experiment where the standard heterogeneous rate constant (k_s) can be calculated with the help of cyclic voltammetry data obtained through the cyclic voltammeter technique in the laboratory environment. It is important to teach students the standard heterogeneous constant at graduate level. Because the students at graduate level know only the chemical reactions and the speeds of these reactions. Hence, they take the events that occur at the surface of the electrode as chemical events. It is essential to have the students comprehend these complex microscopic electrochemical events that occur at the surface of the electrodes. The use of azobenzene (Fig. 1) is important in terms of the applicability of the experiment, since it is cheap and easy to find.

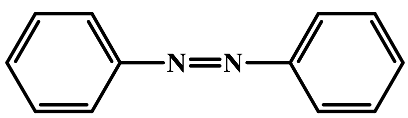

Fig. 1. Structure of azobenzene

There are many studies in the literature where electrochemical experiments were suggested as well as various applications are made[1-4]. In studies, which included cyclic voltammetry experiments, voltammograms were examined and the data obtained from these voltammograms were evaluated. The conclusions of these evaluations were used in the explanations of the electrode reactions of various substances. Among the studies related to education, there were very few examples involving the calculation of (k_s).

EXPERIMENTAL

Dimethyl sulfoxide was used as 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 material in non-aqueous media. The supporting electrolyte, tetrabutylammonium tetrafluoraborate (TBATFB) was purchased from Fluka 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 dimethyl sulfoxide containing 0.1 M TBATFB. The voltammetric experiments were carried out using a computer controlled electroanalysis system which is BAS 100B. A three electrode combination system was used. Platinum electrode and 100 µm platinum electrodes were used as a working electrode. The reference electrode was a silver wire in contact with 0.1 M $AgNO_3$ in dimethyl sulfoxide. The number of electrons transferred and diffusion coefficients were deter-mined by the conventional cyclic voltammetry and ultramicro platinum electrode cyclic voltammetry technique of Baranski[5]. The standard heterogenous rate constants were calculated according to Klingler-Kochi method[5].

Method: The number of electrons transferred and diffusion coefficients were determined by the ultramicro electrode cyclic voltammetry technique of Baranski[5]. The standard heterogeneous rate constants were calculated according to Klingler-Kochi method[5]:

Characterization of the electrode reactions: Cylic voltammograms of the solution containing 1×10^{-3} M of compound in DMSO containing 0.1 M tetrabutyl-ammonium tetraflurorborate at a scan rate 100 mV/s are shown in Fig. 2. The one cathodic peak present at -1567 mV and this is one corresponding anodic part at -1481 mV. During the characterization of the electrode reaction, the following points were analyzed.

Determination of the characteristic of the current: The log i_p *vs.* log v are given in Fig. 3 for each compound. The slopes of these graphs fall in the range, 0.44 ± 0.303 for compound. The results indicate that the adsorption phenomenon is not dominant. The fact that no pre and post peaks are observed in the cyclic voltammograms of compound at high scan rates is another indication that adsorption does not occur, to a considerable extent, on the electrode surface[5]. The Nicholson-Shain criteria state[5-7] that the linear change of the current with $v^{½}$ is an indication that reaction is diffusion controlled can be seen in Fig. 3.

Klingler-Kochi method for the determination of the heterogeneous electron-transfer standard rate constant: In the literature, looking at the standard heterogeneous speed constant values, it is possible to determine whether the electrode reactions are reversible, irreversible or semi-reversible. It is identified that for the reversible reactions, the standard heterogeneous speed constant should be equal to or greater than 0.23 $v^{½}$ cm/s. For the semi-reversible reactions, it should be between 0.23 $v^{½} \geq k_s \geq 0.004$ $v^{½}$ cm/s and for the irreversible reactions, it should be smaller than[5] 0.004 $v^{½}$. After this knowledge was shared with the students, in order to test the reversibility, irreversibility and semi-reversibility of the system, the k_s calculations were made as the following indicates:

The k_s values of the azobenzene, which was calculated according to the Klingler Kochi technique (eqn. 3), were transferred to the graph considering the square root of the scanning speed. The average of the values of k_s, which were independent from the scanning speed at the high scanning speeds, was taken and the standard heterogeneous speed constant was calculated. Fig. 4 displays the obtained k_s- $v^{½}$ curve belonging to azobenzene.

The (k_s) values of the reduction peak of azobenzene being within the interval of 0.23 $v^{½} \geq k_s \geq 0.004$ $v^{½}$ cm/s indicates that the system is semi-reversible[6].

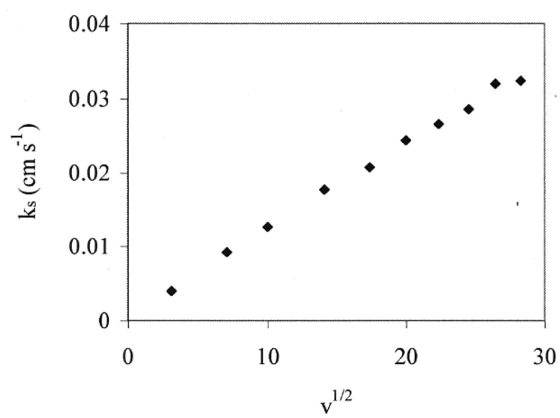

Fig. 4. Exchange of the heterogeneous speed constant of the reduction peak of azobenzene with $v^{½}$

$$k_s = 2.18\left(\frac{D\beta nFv}{RT}\right)^{½} \exp^{\frac{-\beta^2 nF}{RT}\Delta E_p} \qquad \beta = 1,857\frac{RT}{nF(E_p{}^{c} - E^{c}_{p/2})} \qquad (3)$$

In eqn. 3, $\Delta E_p = E_p{}^{c}$-$E_p{}^{a'}$.

In the above formula, D is the diffusion coefficient; β is a constant number; n is the number of electrons transferred to the surface of the electrodes; F is the Faraday Constant 96487 C, v is the scanning speed, R is a constant number 8.314 J/molK and T shows the heat (K).

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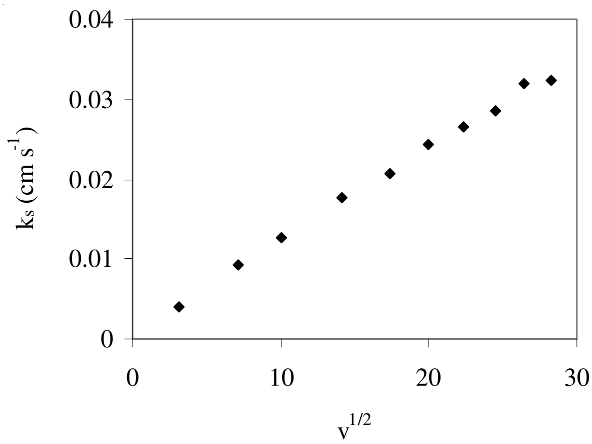

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The n and D, which were calculated with the help of the equation developed by Baranski and the k_s values, were calculated using the Kilngler Kochi equation are given on Table-1.

RESULTS AND DISCUSSION

In this study, a student experiment was suggested in order to have the students comprehend the heterogeneous speed constant. Before doing this suggested experiment at the laboratory, students should be asked to research the literature where the electrochemical behaviours of the azobenzene, the k_s value of which was to be calculated, are analyzed. The literature search and investigation aims to have the students obtain the following basic knowledge regarding azobenzene and how it behaves in similar or different environments other than the environment to be used. The following paragraph summarizes the knowledge they could attain about the general and electrochemical characteristics of azobenzene.

Heterocycles are mainly used in disperse dye chemistry as diazo or coupling components and numerous heterocylic colourants are widely marketed. In addition, new application appeared such as photodynamic therapy, laser industry or reprographic technology[10-13]. The heterocyclic azo dyes are important substances in many industrial processes aiming at, for example, the production of dyes or drug used in chemotherapy[14,15]. These are widely used in industry as textile dyes, colouring agents in foods and pharmaceuticals[16,17]. A number of azo dyes exhibit genotoxic or ecotoxic properties leading to the need for sensitive analytical methods for their determination[18].

The literature search is important as it enables the students to attain knowledge about the substance they would use as well as the electrochemical method before the experiment is done, to comprehend the importance of the studies done in the light of scientific studies and to feel themselves as scientist. There are studies in the literature on the electrochemical behaviours of azobenzene in the non-aqueous environment[19]. In addition to the subject substance and the subject method, it is also important for the students to attain knowledge on k_s calculation, which is the basic topic of this study, by searching the related literature before starting the experiment[6]. The literature analysis should be followed by the discussion and explanation of the concepts, which were unfamiliar to the students, with the instructor. Then, students would have the chance to compare and contrast the results obtained at the literature where the electrochemical characteristics of azobenzene were determined in the non-aqueous environment, with the conclusions of the experiment. The literature analysis is very important for the students in terms of the evaluation of the data obtained during the experiment. Having discussed the studies in the literature with the instructor, students could calculate the k_s values using the experimental data they obtained. The D and n values, which are the other quantities required for the calculation of the k_s value, could be calculated with the help of the suggested experimental steps in the literature. This study aims to teach students the k_s value in electrochemical reactions using the concepts and literature discussed with the instructor as well as following the given experimental steps.

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