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Polarographic and voltammetric investigation of 6′-butoxy-2,6-diamino-3,3′-azodipyridine

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Abstract

Voltammetric and polarographic reduction on a hanging mercury electrode in aqueous-ethanol medium was performed for the 6′-butoxy-2,6-diamino-3,3′-azodipyridine by using SWV, DPP, DCP and CV techniques. Electrochemical behaviour of the azo compound has been investigated depending on ethanol–water ratio. From the polarographic and voltammeric data, electrochemical reduction mechanism has been suggested. Adsorption effect of the azo compound was investigated at different pH values. Optimum conditions are given for its polarographic and voltammetric determination. The limit determination using an HMDE was around 2.72×10^{-9} M for SWV.

Keywords: Azo dyes; Polarography; Voltammetry; Reduction mechanism

1. Introduction

Aromatic azo compounds constitute a very important class of organic compounds because of their widespread applications in many areas of technology and medicine. They are well known for their use as analytical reagents, in dye industry or as chemotherapeutic drugs [1–3].

Only a few heterocyclic dyes derived from azobenzene and containing an amino and pyridine groups conjugated with the aromatic system have been reported. The presence of conjugated bond system and chelating moiety gives rise to a considerable shift of the polarographic and voltammetric peak potentials and currents. Therefore such compounds can be used as metallochromic indicators. Electrochemical methods such as polarography and voltammetry are sufficiently informative tool for studying protolytic equilibria of compounds having a conjugated bond system in different solution media. It is known that *N*-substituted aminoazobenzenes can undergo protonation at the amino, pyridine and azo group. Proton addition induces reorganization of the conjugated bond system, so that different forms indicate different polarographic and voltammetric peak potentials and currents [4–12].

In this study polarographic and voltammetric behaviour of 6′-butoxy-2,6-diamino-3,3′-azodipyridine was investigated. The aim of this study is to explain the electrochemical reaction mechanism for the azo compound using square wave voltammetry (SWV), differential pulse polarography (DPP), direct current polarography (DCP) and cyclic voltammetry (CV) in different media. At the same time, the ionization constants were determined from the pH dependences of the electrochemical measurements and protolytic equilibria of the compound having a conjugated bond system in aqueous-ethanol medium. This compound has not hithetro been investigated by polarographic and voltammetric methods. The molecular structure of the azo compound is given as below (Scheme 1).

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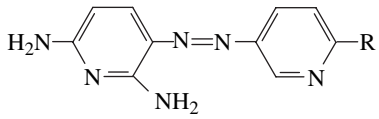

R : $-OCH_2CH_2CH_2CH_3$

Scheme 1.

2. Experimental

6′-Butoxy-2,6-diamino-3,3′-azodipyridine (BADP) was obtained from Aldrich and was used without further purification. Boric acid, phosphoric acid, acetic acid and sodium hydroxide for Britton Robinson buffer were obtained from Merck product. All solutions were prepared using ultra pure water obtained by passing deionized water through a Milli-Q water purification system.

SWV, DPP, DCP and CV polarograms and voltammograms of the azo compound were recorded with a Metrohm VA 757 Computrace Electrochemical Analyser. A three electrode combination system was used. This consisted of a Multi Mode Electrode (DME, SMDE and HMDE), a Ag/AgCl reference electrode and a Pt wire auxiliary electrode. Pulse height of 50 mV and step height of 4 mV were used.

Solutions were degassed with nitrogen for 300 s prior to measurements and for an additional 5 s before each scan. A nitrogen atmosphere was maintained throughout the experiments. Each scan was done on a separate mercury drop at room temperature.

3. Results and discussion

The polarograms and voltammograms of the solution containing 3.85×10^{-6} M of the azo compound were taken in BR buffer solutions containing 50% ethanol at pH values between 2.0 and 12.0. BADP has one electrochemically reducible group that is azo group and its structure is shown in Scheme 1. Differential pulse polarograms and square wave voltammograms of 3.85×10^{-6} M BADP in BR buffer at different pH values are shown in Fig. 1. As shown in Fig. 1, peak currents and potentials are dependent on pH.

Differential pulse polarography and square wave voltammetry of the azo compound give one well-defined polarographic reduction peak I_c at the SMDE and HMDE at a sweep rate of 4 mV/s for DPP and 200 mV/s for SWV in aqueous-ethanol buffers in the pH range 2.0–10.0. The shape of peak I_c became broad at higher pH for DPP and SWV polarograms and voltammograms. The peak potential (E_p) of reduction peak I_c for the azo compound is dependent of pH in the pH range 2.0–12.0 studied as shown in Figs. 1 and 3.

Plots of peak potential (E_p) versus pH for 3.85×10^{-5} M of BADP are depicted in Fig. 2 for DPP and SWV. As the pH was gradually increased, the peak potential shifted towards more negative values.

As shown in Fig. 2, the dependence of the peak potentials of the BADP for SWV and DPP shows a break at a pH value of about 9.5–10.5. Below this value, a proton transfer precedes the electrode process above pH 10.5 the peak potentials are little pH dependent.

Generally the polarographic and voltammetric reduction of an organic compound can be represented by [13–16]:

$$O + aH^+ + ne^- = RHa$$

The approximate relationship between E_p and pH for a reversible reaction at 25 °C is:

$$E_p = E^0 - 0.059(a/n)\,\mathrm{pH}$$

A plot of E_p against pH should be linear with a slope of $0.059a/n$ and an intercept corresponding to E^0 [17,18]. The linear pH dependence of the peak potential for SWV and DPP is given in Table 1.

The equations (Table 1) show that protons participate directly in the reduction process at pH 2.0–11.0. Fig. 2 indicates that the peak potential of the azo compound is constant at pH > 11.0 for DPP and SWV.

Protonation or deprotonation of the N atom in the aniline and pyridine groups is fast. Formally as shown in

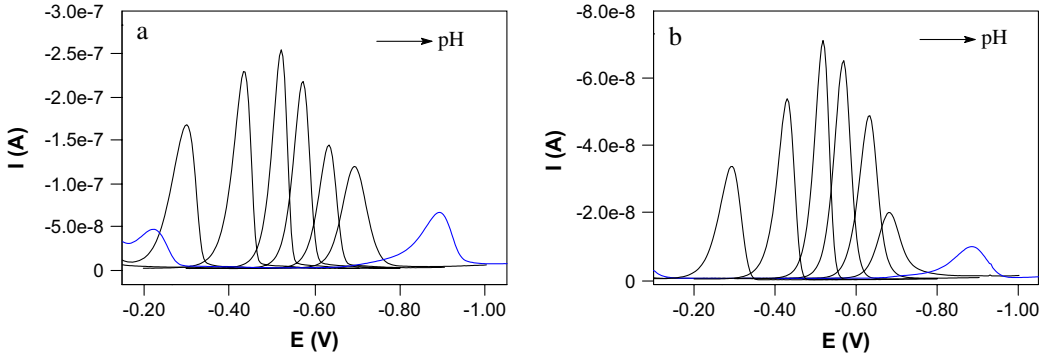

Fig. 1. (a) SWV (3.08, 5.03, 6.34, 7.09, 8.02, 9.36, 11.49) and (b) DPP (3.08, 5.03, 6.34, 7.09, 8.02, 9.36, 11.18) voltammograms and polarograms.